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RUBBER CHEMISTRY AND TECHNOLOGY

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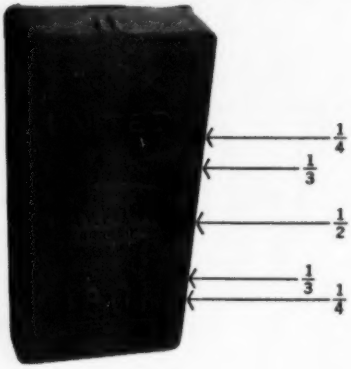

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Rubber Chemistry and Technology is published under the supervision of the Editor, representing the Division of Rubber Chemistry of the American Chemical Society. One object of the publication is to render available in convenient form under one cover important and permanently valuable papers on fundamental research, technical developments, and chemical engineering problems relating to rubber or its allied substances. Another object is to publish timely reviews.

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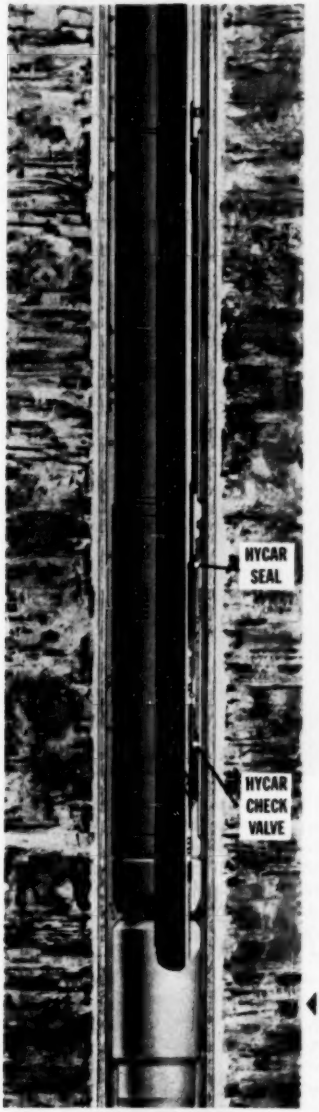

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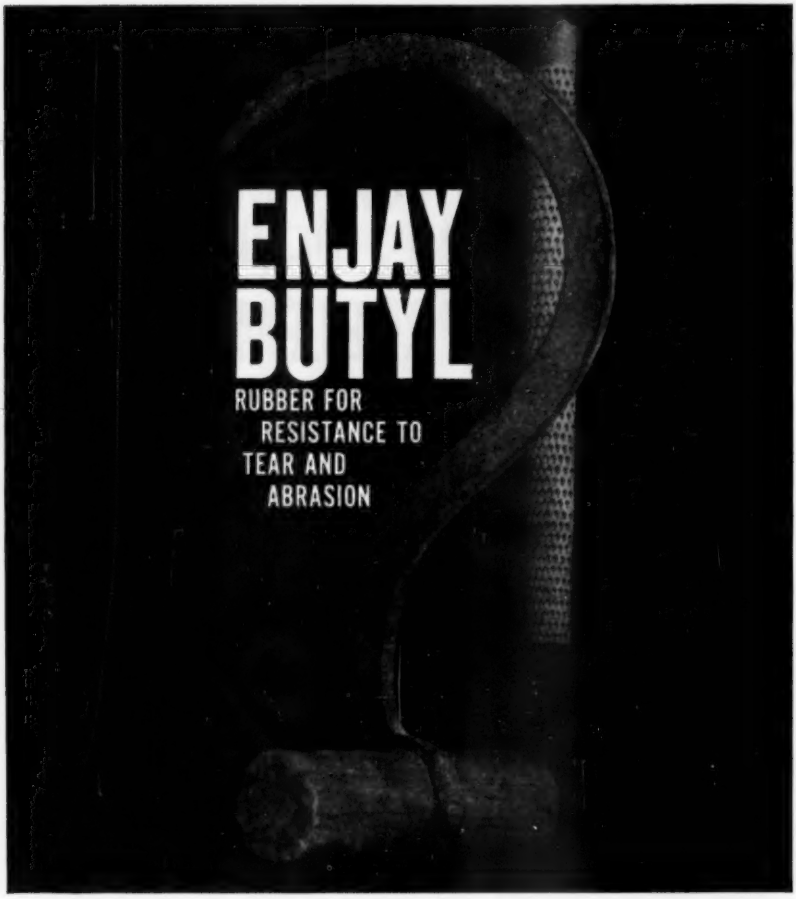

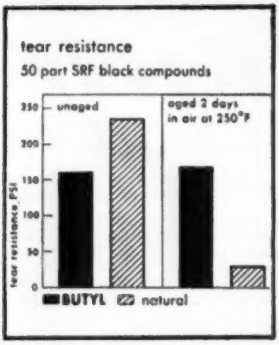

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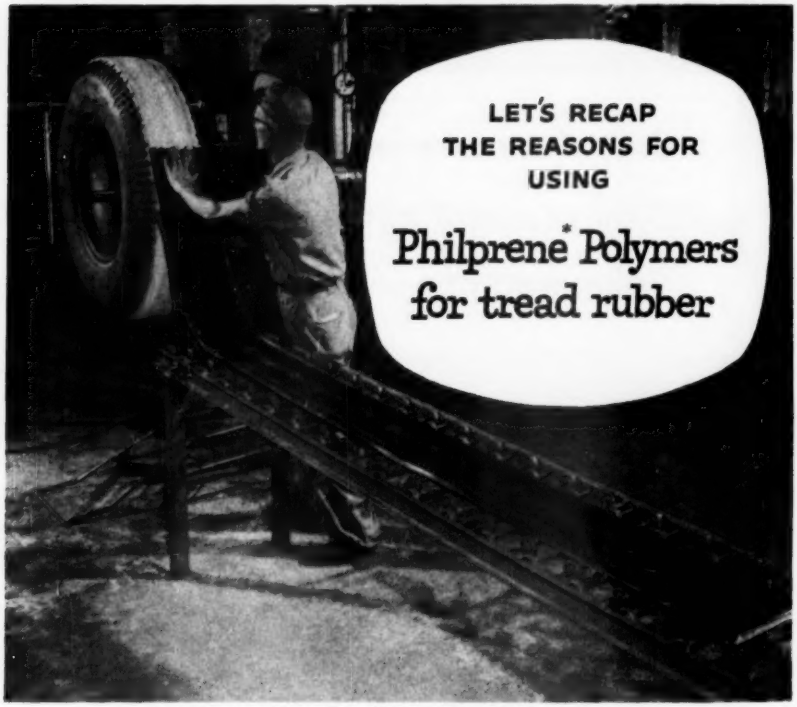

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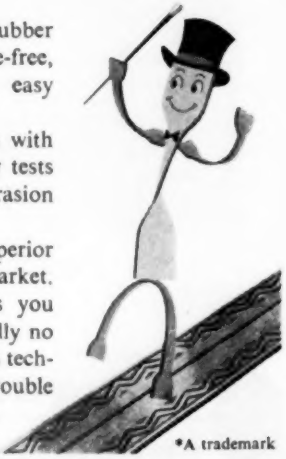

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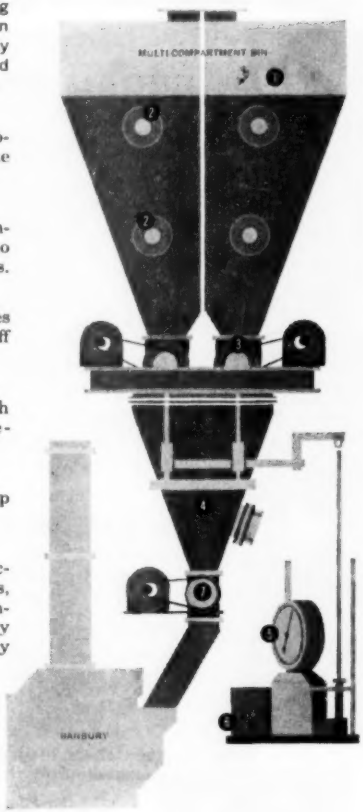

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VOLUME XXXIII • NUMBER FOUR

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1961	Fall	Chicago	Sherman	September 5–8
1962	Spring	Boston	Statler	April 24–27
1962	Fall	Cleveland	Cleveland	October 16–19
1963	Spring	Toronto	Royal York	May 7–10
1963	Fall	New York	Commodore	September 10–13
1964	Spring	Detroit	Cadillac	April 28–May 1
1964	Fall	Chicago	Sherman	September 1–4

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NEW BOOKS AND OTHER PUBLICATIONS

PLASTICS ENGINEERING HANDBOOK of The Society of the Plastics Industry, Inc. Third Edition. Cloth, 7¼ by 10¼ inches, 565 pages. Published by Reinhold Publishing Corp., New York, N. Y. Price: $15.00.—This third edition of the "Plastics Engineering Handbook of The Society of the Plastics Industry, Inc.", is a revised, expanded, up-to-date reference on plastics materials, methods, and fabrication. This new edition adds the advances made since 1954, advances so numerous that the handbook now appears in a larger, double-column format. There is much new material on nomenclature, cellular plastics, decorating, welding, and plastics as adhesives. The book describes practically every step in the manufacturing operation and includes the experience and know-how of more than 200 technicians and authorities. The text is fully illustrated with hundreds of photographs, tables, and charts. Some of the charts alone provide data which should be of value to the plastics plant. This definitive guide to the plastics industry contains considerable current information.

This reviewer suggests that a book of this nature in the form of a rubber engineering handbook also is needed by the industry. [From *Rubber World.*]

ASTM STANDARDS ON PLASTICS (with Related Information). Eleventh Edition (1960). American Society for Testing Materials, Philadelphia, Pa. Hard bound, 9 by 6 inches, 1242 pages. Price: $9.00; to members, $7.20.—The increase in size of this new edition of the Compilation of Standards on Plastics reflects the rapidly growing pace of the plastics industry. This edition contains a total of 213 standards, of which 22 are entirely new, and 23 have been revised or changed in status. In addition to all of the standards prepared by ASTM Committee D-20 on Plastics this book includes selected standards from other committees, which should be of interest to those in the plastics field. Among the topics covered are Specifications for Molding Compounds and Base Materials; Standard and Molded Shapes; Mechanical Properties of Plastics; Effects of Radiation; Thermal Properties of Plastics; Optical Properties of Plastics; Permanence Properties of Plastics; Analytical Methods for Plastics; Molds and Molding Processes for Plastics; Definitions and Nomenclature of Plastics; Conditioning of Plastics; Electrical Insulating Materials; Rubber and Rubber-Like Materials; Adhesives; Color and Gloss Tests; and Miscellaneous Subjects. [From *Rubber World.*]

ASTM STANDARDS ON RUBBER PRODUCTS (with Related Information). American Society for Testing Materials, Philadelphia, Pa. Hard bound, 9 by 6 inches. 1052 pages. Price: to members, $7.80; others, $9.75.—This nineteenth edition of the D-11 compilation is more than 10% larger than the last edition published in May, 1958. The 163 standards include 22 that are completely new and 66 that have been revised or changed in status. Among the new standards are several covering cellular materials of poly(vinyl chloride) or copolymers and urethane foam, two on the effects of radiation, one on abrasion resistance of rubber soles and heels, one on testing automotive air conditioning hose, and several on carbon black. Selected topics include the following: Chemical Tests of Vulcanized Rubber; Physical Tests of Vulcanized Rubber; Electrical Tests; Aging and Weathering Tests of Rubber; Low-

Temperature Tests of Rubber; Automotive and Aeronautical Rubber; Packing and Gasket Materials; Hose and Belting; Tape; Electrical Protective Equipment; Insulated Wire and Cable; Hard Rubber; Latex Foam; Sponge and Expanded Cellular Rubber; Synthetic Elastomers; Compounding Materials; and Nomenclature and Definitions. [From *Rubber World.*]

PRACTICAL LATEX WORK. H. J. Stern. With foreword by Royce J. Noble. The Blackfriars Press, Ltd., Leicester, England. Reprinted in 1957, Third Edition, 1955. Board cover, 4¾ by 7½ inches, 96 pages, illustrated. Price: $2.50.—This book was previously reviewed in *Rubber World,* February, 1956, page 716, but this reprinting is not available from *Rubber World.* [From *Rubber World.*]

THE RUBBER MANUFACTURING INDUSTRY. Compiled by A. T. Mathyoo. Association of Rubber Manufacturers in India, 57-B, Free School St., Calcutta 16, India. Hard bound, 8½ by 5¾ inches. 194 pages.—This book contributes to the application of science and technology to industry by imparting to the junior rubber technicians of the hundreds of rubber factories in India some fundamental technical information on the raw materials and their use in compounding. The book also gives a rapid survey of the processes involved in the manufacture of a number of selected rubber goods. The statistical data and other information on the Indian rubber manufacturing industry contained in this book should prove of considerable value to many others connected with or interested in this industry.

The book describes the origin and development of the rubber industry in India. It lists the names of manufacturing plants and their products and the membership of the Association of the Rubber Manufacturers in India. The chapters on technology are illustrated, including a chapter dealing with testing and testing equipment. [From the *Rubber World.*]

NEUES GUMMI ADRESSBUCH, 1959–60. Third Edition. Published by Curt R. Vincentz Verlag, P.O.B. 8, Hannover, Germany. Linen, 8¼ by 6 inches, 608 pages. Price: DM 32.—The third edition of the New Directory for the German Rubber Industry follows the arrangement of the second edition, published in 1955, but has been completely revised and enlarged. Like its predecessor, the new directory covers manufacturers, dealers, suppliers of raw materials, importers, and sales representatives of foreign firms in the rubber and asbestos industry as well as manufacturers in the allied plastics, cable, and belting fields. The major part of the work consists of an alphabetically arranged geographical index of firms, giving details as to bankers, line of business, etc. There is also, besides an index of companies and list of associations, a buyers' guide with trade marks and brand names including almost 6000 entries. This guide is divided into several parts covering raw materials, semi-manufactures, and finished goods, equipment, testing apparatus, and accessories. A separate section dealing with manufacturers of rubber and plastics machinery and equipment completes this useful directory of the German rubber and allied industries. [From *Rubber World.*]

POLYMER. Vol. 1, No. 1. Butterworth Publications, Ltd., London, W.C.2, England. March, 1960. 124 pages. Annual subscription: $15.00 (£5).—This new quarterly has been founded to provide an international

medium for the publication of original papers on the chemistry, physics, and application of polymer research, and on other disciplines which contribute to the development of polymer science. A substantial research effort is now devoted to this field, and it is felt that the number of papers written has become so large as to justify a journal for their publication.

A feature of the journal will be the publication of short communications dealing with work which merits publicity before a full paper can be prepared and published. These communications, like the papers, will be edited by working editors of wide experience. Manuscripts are invited for publication. Contributions should be sent to the editors, "Polymer", 4–5 Bell Yard, London, W.C.2, England. [From the *Rubber World*.]

CLASSIFICATIONS OF HIGH POLYMERS: A REVIEW. Prepared for the Plastics and High Polymers Division of the Applied Chemistry Section of the International Union of Pure and Applied Chemistry by R. Houwink with the collaboration of H. Bouman, Butterworth and Company (Canada) Ltd., 1367 Danforth Avenue, Toronto 6, Canada. 54 pages. Price: $2.25.—From the Introduction: "One of the problems which the High Polymers Division of the International Union of Pure and Applied Chemistry has been studying is the possibility of drafting a classification system for high polymers covering the field of plastics, rubbers and synthetic fibers.

After preliminary discussions a start was made in 1953 in comparing existing systems and the present report gives a critical and objective review of all the systems both published and unpublished of which the writer is aware.

The review was circulated in draft form to the various individuals responsible for each of the twenty-seven classification systems mentioned and valuable comments were obtained from them which were used in preparing the final version of the review. For general considerations concerning basic classification principles the writer is indebted to Mayer, Bouman, Kappelmeier, de Hoek and Wijbrans, and reference may also be made to Wolf". The "Contents" follow.

1. Introduction
2. Who Needs Classifications?
3. The Different Classification Systems
4. How Various Requirements May Be Covered
5. Critical Discussion of the Existing Classification and Labelling Systems

Introduction

Group A: Classifications Based on the Chemical Structure of the Polymer

(1) The Lepsius System
(2) The Nitsche and Heering System
(3) The Combined Lepsius-Nitsche-Heering System
(4) The de Gorter Decimal Classification
(5) The Nomenclature of the I.U.P.A.C. Commission on Macromolecules (I.U.P.A.C. nomencl.)

Group B: Classifications Based on the Origin of the Polymer (or on the chemical structure of the monomer(s))

(6) The Universal Decimal Classification (U.D.C.)
(7) The Abbreviated U.D.C.

(8) The Centrale Documentatiedienst inzake Kunststoffen System (C.D.K. System)
(9) The Leuchs System
(10) The Abracadabra System
(11) The System of Bounman, Houwink and Kappelmeier
(12) The Oom System
(13) The Standard Commodity Classification (S.C.C.)
(14) The Interscience System
(15) The I.U.P.A.C. System of Letter Abbreviation (I.U.P.A.C. letter)
(16) The Dawson System
(17) The Surface Coating Resin Manufacturers' System (S.C.R.M. System)

Group C: Classifications Based on Properties or on Quality Specifications

(18) The Nolst Trenite System
(19) The British Standards Institution System (B.S.I. System) and the French System
(20) The Swiss System
(21) The System of the American Society for Testing Materials (A.S.T.M. System)
(22) The German 'Typisierung'
(23) The proposed System of Hoekstra

Comparison of Systems (19) to (23)

Group D: Classifications Especially for Use by Patent Documentalists

(24) The United States Patent Office Classification (U.S.P.O.C.)
(25) The Netherlands Patent Office Classification (N.P.O.C.)
(26) The United Kingdom Patent Office Classification (U.K.P.O.C.)

Group E: Alphabetical Classifications

(27) The Classification of Dubois and de Laire

References

Summary

An abbreviated form of the Dawson System (item (16) above) is given in the next review.

SUPPLEMENT to INFORMATION BUREAU CIRCULAR No. 430 of the Research Association of British Rubber Manufacturers, Shrewsbury, England. Systematic Classification of Scientific, Technological, and Commercial Information on Rubber, July, 1956. Skeleton Version. Research Association of British Rubber Manufacturers, Institut Francais du Caoutchouc, Rubber-Stichting, together constituting the International Committee for Classification of Rubber Information (ICCRI).—Circular 430 issued in February, 1956, included an Appendix in which the system was presented in an abridged form. This has been well received and indications have been detected that an even more drastic abridgment might be acceptable, as giving a bird's-eye view of the scheme and permitting those unfamiliar with the full tables to use it without resorting to detail. An abridgment of this kind would be adequate to the classification of books and of small collections of abstracts.

Such a skeleton abridgment is set forth herewith as a supplement to Circular 430 and is regarded as the irreducible minimum to which the Scheme can be cut down. It does not excuse the user from reading the introduction to the Circular and the Main Tables should still be consulted for explanatory notes.

The Circular itself will be sent gratis to any inquirer while stocks last.

MAIN FRAMEWORK

0. General
1. Plants Producing Rubber; Planting
2. Natural Latex
2S. Synthetic Latex
3. Crude Rubber
3Gutta. Gutta-Percha and like Products
3N. Reclaim from Natural Rubber
3S. Synthetic Rubbers and Like Products
4. Compounding Ingredients
5. Cotton Fibers and Textiles
5A. Other Fibers and Textiles
6. Vulcanized Rubber

    66. Applications; vulcanized rubber goods

7. Works Processes and Materials
8. Machinery and Appliances
9. Economics

0. General; Rubber Industry as a Whole

    015. History

1. Plants; Planting

    1A. Hevea
        1A34. Diseases: pests
        1A56. Tapping

    1B. Guayule
    1C. Kok-saghyz

2. Natural Latex

    23. Properties (A)
    24. Testing (A)
    25. Treatment

        251. Equipment; latex appliances
        252. Coagulation
        253. Concentration
        254. Compounding

    26. Applications

        261. Compositions, including adhesives of latex (A)
        262. Latex deposits (A)

            2626(AZ). Articles made from latex; articles may subsequently be vulcanized (A)

        266. Vulcanized latex (A)

2S. Synthetic Latices Obtained Directly by Polymerization

Types, properties, testing, and applications as 3S; for preparation see $3S_12_1$; subdivide like 2 as applicable.

3. Crude Rubber

31. Preparation
32. Types

3217. Powdered rubber (A)

33. Properties (A)
34. Testing (A)
35. Treatment; processing.

357. Vulcanization

36. Applications

361. Compositions, including solutions and cements (A)

3626(AZ). Crude rubber articles (A)

363. Chemical derivatives of commercial importance (A)

36321. Cyclo-rubbers (A)
36322. Chlorinated rubber (A)
36323. Hydrohalogenated rubber (A)

3Gutta. Gutta-Percha
3N. Reclaim from Natural Rubber (A)
3S. Synthetic Rubbers and like Products

3S1. Manufacture

3S121. Emulsion polymerization

3S2. Types

3S2D. From hydrocarbons (A)

3S2D21MD23. Butadiene/styrene rubbers (A)
3S2D21MN21. Butadiene/acrylonitrile rubbers (A)

3S2E. From acids; acid anhydrides; esters (A)
3S2H. From halogen-containing compounds (A)

3S2M. Condensation and polyaddition polymers (A)
3S2T. From sulphur-containing compounds (A)
3S2Y. From compounds containing inorganic elements not included in other classes

3S2Y21. Silicon compounds

N.B.—The leading synthetics have the following systematic numbers:

Butyl—3S2D25MD22
GR-A—3S2D21MN21
GR-S—3S2D21MD23
Hypalon—3S2D24.6327
Neoprene—3S2H22
Silicones—3S2Y21
Thiokola—3S2T23
Vulcollan—3S2MAEN

3S3. Properties (A)
3S4. Testing (A)
3S5. Treatment (A)
3S54. Compounding
3S6. Applications
3S61. Compositions, including solutions and cements (A)
3S62. Applications in unvulcanized, or thermoplastic form
36626(AZ). Goods (A)
3S66. Applications in vulcanized, or thermoset, form
3S666(AZ). Goods (A)
3SN. Reclaim from synthetic rubbers (A)

4. Compounding Ingredients
42. Types
421. Fillers
421C. Carbon Black (A)
422. Accelerators (A)
423. Antioxidants (A)
424. Pigments; dyes (A)
425. Vulcanizing agents (A)
426. Softeners (A)
42(10). Blowing agents (A)
42(12). Protective agents against deterioration other than by normal aging (A)
43. Properties (A)
44. Testing (A)
45. Treatment in general
46. Application in rubber; reinforcement

5. Cotton Fibers and Textiles (A)
5A. Fibers and Textiles other than Cotton (A)
6. Vulcanized Rubber
63. Properties (A)
6323. Aging
64. Analysis and testing
643. Aging tests
65. Treatment
654. Bonding to other materials
66. Applications
66A. Tires; inner tubes
66A21. Pneumatic tires (A)
66A211. Manufacture
66A2113. Fabric (A)
66A24. Inner tubes (A)

66A3. Properties
66A4. Testing
66A5. Treatment; repair
66A6. Accessories

66B. Belting

66B21. Conveyor (A)
66B22. Power transmission (A)

66C. Cables; electrical insulation
66C21. Cable and wire (A)
66C22. Insulating tape (A)
66C29. Conductive rubber (A)

66F. Footwear

66G. Games; toys; sports accessories (A)

66G21. Balls (A)

66H. Hose; tubing (A)

66M. Mechanical goods not elsewhere specified (A)

66M21. Shock absorbers (A)
66M22. Unions, connections, packings, stoppers (A)
66M23. Abrasives (A)
66M24. Insulation other than electrical (A)
66M25. Printing devices (A)
66M26. Rubber as a general constructional material (A)

66R. Roads; flooring; mats (A)

66R23. Flooring in sheet form (A)
66R27. Rubber compositions for roads (A). (For compositions employing powdered crude rubber, see 3217.6)

66S. Surgical and dental goods (A)

66T. Textile-rubber goods (A)

66T21. Proofed fabric (A)
66T22. Rubber thread and elastic fabric (A)
66T23. Analogous all-rubber articles (A)

66T232222(A). All-rubber gloves (A)

66X. Cellular rubber; miscellaneous soft rubber goods (A)

66X1. Cellular rubber (A)

66X16. Applications (AZ)

66Z. Hard rubber; ebonite (A)

66Z6221. Accumulator parts (A)

7. Works Materials and Processes other than Raw Materials for Working up and Processing Rubber

722. Solvents (A)

72323. Dusting powders (A)

755. Industrial hazards

756. Industrial disease

8. Machinery and Appliances

81. General types

818. Mixing machinery (A)
819. Calendars (A)
81(10). Extruders (A)
81(12). Molds (A)
81(15). Vulcanizers (A)

82. Specific types (AZ)

82A. Tire machinery (A)

82A(10). Tire repair machinery (A)

9. Organization; Commerce; Economics; Statistics

91. Organization
92. Finance
93. Personnel
94. Associations; institutions; companies
95. Law
96. Statistics

966. Vulcanized rubber goods statistics (AZ)

AUXILIARY TABLES

It is clear that raw materials and manufactured goods can all be regarded from the points of view of (1) manufacture and preparation, (2) kinds or types, (3) properties, (4) testing, (5) treatment, and (6) applications. Numbers indicating these points of view are provided in Auxiliary Table A given in skeleton form below. Its applicability is indicated by (A) appearing after a number in the above tables.

Again, raw materials such as latex, rubber, neoprene, or semi-manufactured materials e.g. sponge rubber, can be used in making a variety of goods, and Auxiliary Table AZ below provides a set of symbols for indicating such end use of a particular raw material. Its applicability is indicated by (AZ) after a number.

AUXILIARY TABLE A

.1 Source; origin; preparation; manufacture
.2 Types; trivial notes; history
.3 Properties

.32 Chemical
.34 Physical

.4 Testing

.42 Chemical analysis
.44 Physical testing

.5 Treatment
.6 Applications; accessories

AUXILIARY TABLE AZ

A. Tires
B. Belting
C. Cables
F. Footwear
G. Games; toys; sports accessories
H. Hose; tubing
M. Mechanical goods not elsewhere specified
R. Roads; flooring
S. Surgicals
T. Textile-rubber goods; thread
X. Cellular rubber; miscellaneous soft rubber goods
Z. Hard rubber; ebonite

These auxiliary tables can be combined in a variety of ways, of which a few examples are given herewith.

Thus, consider neoprene, the number for which is 3S2H22. The chemical analysis of unvulcanized neoprene is classified under 3S2H22.42. Hose made of vulcanized neoprene is 3S2H22.666H. The physical properties of hose made of vulcanized neoprene are classified under 3S2H22.666H.3. Cellular rubber made of vulcanized neoprene is 3S2H22.666X1. Soling made of cellular vulcanized neoprene is under 3S2H22.666X16F. The use of the decimal point to separate a compound number into its several parts is often helpful but not essential.

B.R.P.R.A. LIST OF PUBLICATIONS, FIRST SUPPLEMENT, 1959–60

B.R.P.R.A. List of Publications, First Supplement, 1959–60

(For the 1940–1959 list see R. C. & T., 2*nd* issue, 1960)

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IUPAC
INTERNATIONAL SYMPOSIUM ON MACROMOLECULAR CHEMISTRY

Montreal, Canada, July 27–August 1, 1961, Chairman C. A. Winkler

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Canadian High Polymer Forum

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The Canadian High Polymer Forum is the host group and the Division of Polymer Chemistry, ACS and the Commission on Macromolecules of IUPAC are cosponsoring groups. The patrons are the Chemical Institute of Canada, the Canadian Section of the Society of Chemical Industry, and the Canadian Association of Physicists. The address of the Organizing Committee, International Symposium on Macromolecular Chemistry is P.O. Box 816, Sarnia, Ontario, Canada.

The Symposium is the largest, annual meeting of polymer scientists. The meeting in 1961 will be held in the Queen Elizabeth Hotel, July 27–August 1st, 1961.

The Symposium will embrace all aspects of high polymer science with special emphasis on the newer fields of research. Papers of like interest will be grouped and introduced by an invited speaker.

Authors are asked to correspond with the Organizing Committee. Papers may be given in any language but those presented in English will be understood by the majority of the audience. Abstracts will be required.

Plenary lectures and invited lectures are planned. Details will be in a second circular.

Although ample accommodation is available in Montreal those attending are reminded that the meeting is being held at the height of the tourist season. Thus, the Organizing Committee must release unassigned rooms early. To avoid disappointment please indicate your intention to attend. Rooms in the Queen Elizabeth, the Sheraton-Mount Royal and the Laurentian will be available through the Montreal Tourist and Convention Bureau. Firm reservations will be requested in the second circular.

Registration will be required. Details will be given in the second circular. All sessions will be held in the Queen Elizabeth.

Montreal, Canada, may be reached easily by plane, boat or train. Direct transatlantic flights are available from most countries. Frequent connecting plane flights are made to the larger cities in Canada and the United States. Transatlantic ships arrive in Montreal or dock at Montreal on their way through the St. Lawrence Seaway. Montreal is a main terminus for train service. If your travel agency is unable to supply details please contact the Montreal Tourist and Convention Bureau, 2055 Peel Street, Montreal, P.Q., Canada.

It is not the intention of the Organizing Committee to plan an exhibition. However, space is available and those wishing to sponsor exhibits or displays should contact the Director of Sales, Queen Elizabeth Hotel, Montreal, P.Q., Canada.

There will be a Ladies Program and a program of social events and excursions.

The Chemical Institute of Canada will hold its Annual Conference and Exhibition at the Queen Elizabeth, August 3rd and 4th, 1961. For details please write the Chemical Institute of Canada, 48 Rideau Street, Ottawa 2, Ontario, Canada.

The International Union of Pure and Applied Chemistry will hold its Conference and Congress in 1961 in Montreal, the Conference from August 2nd to 5th and the Congress from August 6th to 12th. For details please write the Organizing Committee, IUPAC Congress, National Research Council, Ottawa 2, Ontario, Canada.

Correspondence relating to the International Symposium on Macromolecular Chemistry should be addressed to the Organizing Committee, International Symposium on Macromolecular Chemistry, P.O. Box 816, Sarnia, Ontario, Canada. Cables:—Macromol Sarnia.

ENERGY REQUIREMENTS OF MECHANICAL SHEAR DEGRADATION IN CONCENTRATED POLYMER SOLUTIONS *

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INTRODUCTION

Under certain conditions the molecular weights of polymers are reduced by mechanical shearing in the flow of their concentrated solutions through capillary tubes[1,2]. The energy of reaction for such a polymer degradation process is probably a small positive value if estimated either from the energy of polymerization[3] or from the energies of the chemical bonds broken and made in hypothetical reaction schemes for the process[4]. The energy of activation for such a degradation process must be limited by the bond energy of aliphatic carbon-carbon bonds (about 80 kcal per mole) as the upper limit. This value is in the neighborhood of values around 50 kcal per mole of broken bonds reported by various authors[5–8] for the activation energy of thermal degradation in several different polymers. This paper reports and compares with the foregoing estimates the experimentally observed energy consumption of the mechanical shear degradation process as a function of the following experimental variables: nominal rate of shear, shearing temperature, polymer concentration in solution, and polymer molecular weight.

EXPERIMENTAL PROCEDURES, MATERIALS, AND RESULTS

The solutions of polyisobutenes in *n*-hexadecane investigated and the experimental techniques used here have been described in detail in a previous publication[9] to which the reader is referred. The θ temperature for these solutions has been evaluated[10] as 175° K, but the solvent freezes at 18° C. Column 5 of Table I gives the final viscosity average molecular weights after degradation for the polymers, concentrations, temperatures, and nominal rates of shear listed in the first four columns, respectively, of that table. The shear loads as functions of the number of shearing passes under these conditions have been reported elsewhere[1,4]. Figure 1 shows the shear loads as functions of viscosity average molecular weight at several values of nominal rate of shear, D, under conditions where no shear degradation occurs.

TREATMENT OF DATA

In order to convert the change in viscosity average molecular weight into the number of bonds ruptured, the somewhat drastic approximation is made of using the relation

$$B/AW = (1/\bar{M}_n - 1/\bar{M}_{n_0}) \qquad (1)$$

* Reprinted from the *Journal of Chemical Physics*, Vol. 32, pages 350–356, February 1960. Extracted partly from a thesis submitted to the Graduate School of the University of Maryland in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

TABLE I

ENERGY REQUIREMENT DATA FOR SHEAR DEGRADATION OF POLYISOBUTENE IN *n*-HEXADECANE UNDER VARIOUS CONDITIONS

Vistanex No.	Concentration, wt %	Temperature, °C	Nominal rate of shear, D, sec^{-1}	Final molecular weight, $\bar{M}_v \times 10^{-5}$	Bonds ruptured per cm^3 solution, moles, $\times 10^8$	H, degradation energy area, lb × pass	Degradation energy per mole bonds ruptured, kcal
B—60	10	40	66,000	0.79	1.27	454.9	291,000
($\bar{M}_{v0}$ = 910,000)							
B—80		40	65,600	0.83	1.71	485.2	230,000
($\bar{M}_{v0}$ = 1,020,000)			33,000	0.94	0.639	142.8	182,000
			18,900	1.02	0	—	—
	15	40	66,000	0.74	4.23	907.9	175,000
B—100	5	40	65,600	1.34	0.667	360.0	448,000
($\bar{M}_{v0}$ = 1,750,000)			33,000	1.59	0.221	130.5	478,000
			18,900	1.75	0	—	—
	10	30	65,600	0.90	4.11	1339.0	265,000
			33,000	1.28	1.60	607.2	308,000
			18,900	1.49	0.802	321.5	326,000
		40	65,600	1.13	2.39	966.4	329,000
			33,000	1.41	1.05	393.6	305,000
			18,900	1.55	0.563	239.8	348,000
			9,500	1.75	0	—	—
		50	65,600	1.28	1.60	628.6	319,000
			33,000	1.42	1.01	334.7	269,000
			26,000	1.57	0.502	252.2	408,000
			18,900	1.60	0.414	50.6	99,000
	15	40	65,600	1.00	5.12	1616.0	256,000
				1.02	4.90	1576.3	260,000
				1.02	4.90	1566.6	261,000
			33,000	1.27	2.46	780.1	257,000
			18,900	1.51	1.04	377.3	295,000
	20	40	66,000	0.87	8.79	2653.0	245,000

TABLE I—*Continued*

Vistanex No.	Concentration, wt %	Temperature, °C	Nominal rate of shear, D, sec^{-1}	Binal molecular weight, $\bar{M}_v \times 10^{-6}$	Bonds ruptured per cm^3 solution, moles, $\times 10^8$	H, degradation energy area, lb × pass	Degradation energy per mole bonds ruptured, kcal
B—120 ($\bar{M}_{v0} = 1{,}900{,}000$)	10	40	66,000	1.20	2.34	970.0	337,000
B—140 ($\bar{M}_{v0} = 2{,}520{,}000$)		20	66,000	0.76	6.99	3315.0	385,000
		30	66,000	0.94	5.07	2125.1	340,000
		40	65,600	1.40	2.34	1384.0	481,000
			33,000	1.83	1.13	512.6	368,000
			18,900	2.16	0.502	262.0	424,000
		50	66,000	1.49	2.08	785.7	307,000
		60	66,000	1.58	1.80	616.9	278,000
		70	66,000	1.75	1.32	515.1	316,000
		80	66,000	2.09	0.616	395.3	521,000
	15	40	66,000	1.06	6.23	2647.9	345,000

where B is the number of bonds ruptured, A is Avogadro's number, W is the weight of polymer sample, and $\bar{M}_{n_0}$ and $\bar{M}_n$ are the initial and final *number* average molecular weights, respectively. Viscosity average molecular weights M_v calculated in this investigation are substituted for the number average molecular weights in Equation (1). This procedure introduces an uncertainty which is dependent on the molecular weight distribution of the undegraded and the degraded polymers. For a polydisperse polymer $\bar{M}_v$ is always greater than $\bar{M}_n$. Therefore if the form of the molecular weight distribution remained unchanged during degradation so that the ratio of $\bar{M}_v$ to $\bar{M}_n$ remained constant, the foregoing procedure would overestimate the number of bonds ruptured and therefore underestimate the energy consumed per rupture. However this conclusion may be affected by a change in the form of the molecular weight distribution during degradation, the possibility of which we now explore.

The form of the molecular weight distribution of polyisobutene samples similar to the undegraded polymers investigated here is given by Van Holde

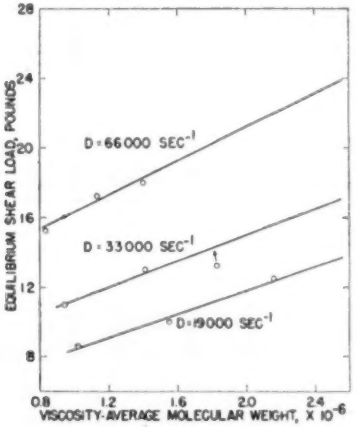

FIG. 1.—Equilibrium shear load in absence of shear degradation as a function of viscosity average molecular weight for 10 wt % B-100 polyisobutene in *n*-hexadecane at 40° and several nominal rates of shear, D, indicated.

and Williams[11]. They are wide and highly skewed. Substantial low molecular weight material is present and a long narrow tail extends to relatively high molecular weights. The effect of shear degradation on this distribution is believed to be to cut off most of the high molecular weight end relatively sharply above a critical molecular weight value. The material which disappears from the high molecular weight end of course reappears at lower molecular weights below this critical value. This interpretation is supported by the incidental fractionation data given in Reference 2. The effect of a high molecular weight tail is to increase the ratio of viscosity average to number average molecular weight. Therefore, the effect of eliminating such a tail in the degradation process is to decrease the ratio of $\bar{M}_v$ to $\bar{M}_n$. This further increases the overestimate of the number of ruptured bonds as obtained by the foregoing procedure. Therefore, the values finally obtained for energy consumed per bond rupture are certainly lower than the true values. However, sample calculations for extreme situations consistent with the extent of degra-

dation observed show that this discrepancy is certainly no greater than a factor of 2 or so. Column 6 of Table I gives the ultimate number of bonds ruptured per cm^3 of solution for all the conditions listed there.

If the plots in Figure 1 are extrapolated to molecular weights higher than those for which data are shown there, estimates are obtained for the equilibrium shear loads which would be obtained for the higher molecular weights if degradation did not occur for them. It is of course impossible to directly observe these equilibrium shear loads for the higher molecular weights since degradation does in fact occur for them. The linear plots shown in Figure 1 are used for these extrapolations because they provide as sensitive a functionality between ordinate and abscissa as can be supported by the experimental data in the figure. These data do not determine any of the more sophisticated functional-

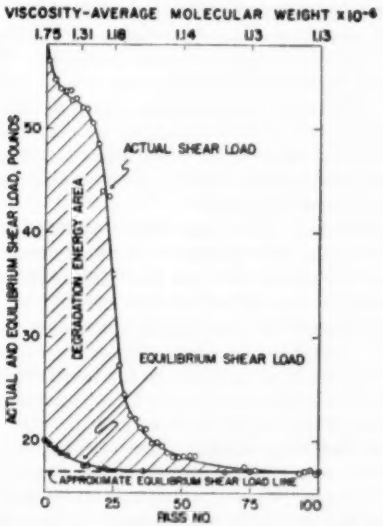

FIG. 2.—Actual and equilibrium shear load as a function of amount of shearing for 10 wt % Vistanex B-100 polyisobutene in *n*-hexadecane at 40° and 66,000 sec^{-1} nominal rate of shear, *D*. Shaded area represents degradation energy. Dashed horizontal line represents approximate equilibrium shear load. The top scale represents the molecular weights existing at the various stages of degradation corresponding to the pass numbers on the bottom scale. (It is in fact a cross plot of the ordinate of Figure 7 in Reference 9.)

ities which have been discussed between molecular weight and viscosity (to which equilibrium shear load should be proportional at a given rate of shear). Representative plots for the observed actual shear load and the estimated equilibrium shear load determined as above are shown in Figure 2, which applies specifically to the shear degradation of a solution of 10 wt % Vistanex B-100 at 40° and 66,000 sec^{-1}.

A large and abrupt increase in observed shear load is seen when a shearing condition where shear degradation occurs is compared with a condition where degradation does not occur (cf. Figures 1, 5, and 7 of Reference 9). This fact suggests[9] the identification of the equilibrium shear load with energy used in the shearing process in actually overcoming viscoelastic resistance to flow as distinct from energy used in the rupture of polymer molecular bonds. This

latter energy is accordingly identified with the difference between the observed and the equilibrium shear loads.

A set of curves such as those shown in Figure 2 applies to a fixed nominal rate of shear. The product of this rate and the shearing stress (proportional to the shear load on the ordinate) gives the rate of energy dissipation. Since pass number is in effect a time coordinate, the area between the observed and the equilibrium shear load curves, shaded in Figure 2, is directly proportional to the energy used in the degradation process and can be converted thereto simply by multiplying by the appropriate proportionality factor.

For a number of conditions represented in Table I data are not available to make the extrapolations, as in Figure 1, necessary to construct an estimated equilibrium shear load plot. To handle these cases, the horizontal line through the final observed shear load (see Figure 2) has been used as an approximate equilibrium shear load curve and a correction applied by comparison of results from the approximate and from the extrapolated equilibrium shear load curves for those conditions for which the latter is available. The average ratio of approximate to actual degradation energy area is 0.97 and the variation from that value is small. Therefore in the cases where actual degradation energy areas are not obtainable, an area is obtained by correcting the approximate area by the factor of 0.97. For all the conditions listed in Table I, Column 7 gives either the actual degradation energy area or the corrected approximate area if the actual area is not obtainable.

The part of the observed shear load which corresponds to energy used in bond rupture does not have the nature of a force overcoming resistance to viscous flow. Therefore the observed shear load data cannot be treated by rheological techniques such as the differentiation method to reduce them to flow curves relating the fundamental rheological quantities of shearing stress and actual rate of shear. Accordingly these quantities cannot be used for any direct estimation of degradation energies or for the conversion of degradation energy area to degradation energy itself. This conversion can, however, be accomplished with completely equivalent results directly from the shear load and the geometry of the instrument. The result gives the average value throughout the capillary which is the same average as obtained for the number of bonds ruptured. However, since the shearing stress and rate of shear change with radial position in the capillary, the energy consumption at any particular position in the capillary may differ correspondingly from this average.

The cross-sectional area of the piston to which the shear load is applied is 1.307 cm^2. Therefore in each pass, the energy corresponding to 1 cm of piston travel is supplied to 1.307 cm^3 of polymer solution. Since a pound of force is equal to 444,822 dynes, each pound of shear load applied to the piston corresponds in each pass to (444,822 dyne cm cm^{-1})/(1.307 cm^3 cm^{-1}) (4.184 $\times$ 10^{10} erg $kcal^{-1}$) = 8.12 $\times$ 10^{-6} kcal per cm^3 of solution. For all the conditions represented in Table I, Column 8 gives the degradation energy per mole of bonds ruptured.

DISCUSSION

The result for 10% B-100 Vistanex at 50° and 18,900 sec^{-1} is out of line with the other degradation energies. The result at this condition in the kinetic analysis of the degradation process[1] is also discordant. Apparently an undetected error has entered the results at this condition.

An indication of the reproducibility of the results is given by the three values listed for 15% B-100 Vistanex at 40° and 65,600 sec^{-1}. These are results for independent repeated degradations for these conditions.

TABLE II

DEGRADATION ENERGY

Concentration wt %		5				10				15	20
Temperature ° C		40	20	30	40	50	60	70	80	40	40
Viscosity average molecular wt—$\bar{M}_v$ $\times 10^{-3}$	Nominal rate shear D sec^{-1} $\times 10^{-2}$	(kcal/mole bonds ruptured) $\times 10^{-3}$									
0.91	66				291						
1.02	66				230					175	
	33				182						
1.75	66	448		265	329	319				260	245
	33	478		308	305	269				257	
	26					408					
	19			326	348	99				295	
1.90	66				337						
2.52	66		385	340	481	307	278	316	521	345	
	33				368						
	19				424						

Table II suggests the amount of shear energy used in degradation to be nearly independent of nominal rate of shear and of temperature, to decrease with increasing concentration, and to increase with increasing original molecular weight. More extensive measurements[12] at 80° where the degradation is becoming less severe than at lower temperatures, suggest that the degradation energy increases as temperature rises into the range of less severe degradation. These variations probably represent variations in the respective amounts of the stored free energy in the bonds or macromolecular chains surrounding a ruptured bond which are dissipated with and without contributing to overcoming viscoelastic resistance to flow when the bond ruptures.

The immediately outstanding feature of the results is that the energy dissipated in rupturing a bond is several thousand times the bond energy. No explanation of this behavior has been found in terms of the energy of reaction. A sensible explanation can be proposed, however, in terms of the energy of activation for the degradation process.

As discussed previously[1] the bond rupture in mechanical shear degradation is considered to be activated by energy supplied from the mechanical shearing forces and temporarily stored in the bonds during the small but finite times required for the occurrence of the individual inter- and intramolecular motions which collectively constitute the viscoelastic shearing process. The increased potential energy of the bonds associated with this storage is conceived to be more than just the barriers to internal rotation of bonds within macromolecules. The configurational changes of the macromolecular chains can be accounted for entirely by internal rotation. However, it is considered unlikely that the actual process of deformation proceeds exclusively by internal rotation at all stages. The end result may be energetically equivalent to pure internal rotation. However, during the actual occurrence of the deformation it is likely that bond length stretchings and bond angle distortions occur as well as internal rotations. The stretchings and distortions raise the potential energy while they exist and provide a means of activating mechanical bond rupture. As time elapses for internal rotation to occur sufficiently to completely accomodate the deformation, the high energy bond conditions relax and the net effects are those of internal rotation.

Upon the completion of an individual inter- or intramolecular movement the

free energy temporarily stored during the movement as potential energy in the interatomic bonds involved in the movement becomes stored as reduced entropy of deformation of the polymer chain molecules. In the equilibrium static deformation of polymers the major part (say 85%[13]) of the stored free energy is in the form of reduced entropy of deformation. It is clear, however, that the only part of the stored free energy which can activate bond rupture is that in the form of potential energy in the bond-to-be-ruptured. No mechanism is conceivable by which reduced entropy of deformation of the molecular chains can raise the energy of an individual interatomic bond as would be necessary to activate rupture.

In order to accumulate sufficient energy in a bond to activate its rupture, however, it is considered that free energy introduced by the shear field into many bonds or macromolecular chains is concentrated into the bond-to-be-ruptured through any of several types of interatomic connections in crude analogy with the combination of tensions in entangled strings. In this process the only function of the stored free energy is to produce tension in the macromolecular chains so both potential energy stored in individual bonds and reduced entropy of deformation stored in the chains can be effective.

Consider that free energy which is temporarily stored in those unruptured bonds and macromolecular chains involved in concentration energy into the ruptured bond. It may be dissipated upon rupture without contributing to overcoming viscoelastic resistance to flow. If so, all the energy so dissipated would be included in the energy consumed in the rupture process. This quantity would then be in no way limited by the energy actually required to activate the rupture of the ruptured bond. In this case the energy consumed can give some rough information about the number of bonds or macromolecular chains involved in concentration energy into the ruptured bond.

Such information cannot be very definite since it is impossible to know reliably the amount of energy temporarily stored in the individual bonds or macromolecular chains involved in concentrating energy into the ruptured bond. It is also impossible to know what portion, if any, of the energy so stored is used after rupture to help overcome viscoelastic resistance to flow. However, some limits may be set.

Since a flow process involves continuous shearing, polymer molecules present find no static equilibrium deformed condition and continuously perform inter- and intramolecular movements in reaction to the continuous shearing. It is during the occurrence of these movements that free energy is stored as potential energy in individual bonds. Therefore in a flow process the stored free energy should include a greater proportion of potential energy than it does for equilibrium static deformation mentioned earlier. For a flow process no means of analysis has been devised to evaluate the relative division of the stored free energy between potential energy in bonds and reduced configurational entropy of deformation. However, it appears that both possibilities probably make substantial contributions.

A reasonable procedure seems to be first to consider the two extreme cases where (1) all the stored free energy is reduced configurational entropy of deformation and (2) all the stored free energy is potential energy in bonds. Subsequently the existing balance of the two cases can be considered. Let us assume that all the stored free energy involved in concentrating the required energy of activation into a bond-to-be-ruptured is dissipated at the time of rupture without contributing to overcoming viscoelastic resistance to flow. This assumption will promote a minimum estimate for the number of bonds or

macromolecular chains involves in concentrating energy of activation into a bond-to-be-ruptured.

Storage completely as configurational entropy of deformation.—The kinetic theory of rubber elasticity provides a means of calculating the free energy associated with the reduction of configurational entropy by deformation of a section of a macromolecule between two adjacent entanglements with other macromolecular chains. For large deformations the force f on a chain macromolecular section containing n links each of length l, and whose ends are held a distance r apart is given in the Langevin approximation[14] as

$$f = (kT/l)\mathcal{L}^{-1}(r/nl) \tag{2}$$

where T is absolute temperature, k is the Boltzmann constant, and $\mathcal{L}^{-1}(r/nl)$ is the inverse Langevin function defined by

$$(r/nl) = \coth \mathcal{L}^{-1}(r/nl) - 1/\mathcal{L}^{-1}(r/nl) \tag{3}$$

For each section the corresponding energy stored E in going from the undeformed to a deformed condition is

$$\begin{aligned} E &= \int_{r_0}^{r} (kT/l)\mathcal{L}^{-1}(r/nl)dr \\ &= \int_{(r/nl)_0}^{(r/nl)} (kT/l)\mathcal{L}^{-1}(r/nl)d(r/nl)nl \\ &= \int_{(r/nl)_0}^{(r/nl)} (kTn\mathcal{L}^{-1}(r/nl)d(r/nl) \end{aligned} \tag{4}$$

The quantity r_0 is the most probable distance between ends for the undeformed macromolecular section and[15] from Reference 13,

$$(r/nl)_0 = (r_0/nl) = (l/nl)(2n/3)^{\frac{1}{2}} = (2/3n)^{\frac{1}{2}} \tag{5}$$

For polyisobutene, measurements of viscosity as a function of molecular weight indicate that the molecular weight between chain entanglements is about 17,000 for the undiluted polymer[16–17]. If the polymer is diluted with solvent the molecular weight between entanglements varies inversely with the volume fraction of polymer[17]. For the present 10 wt % solutions the value is then about 150,000. For the purposes of calculation we assume that each monomer unit of base molecular weight 56 constitutes a chain link. The number n of links between entanglements for the present case then becomes about 2700. Inserting n = 2,700 into Equation (5) gives $(r/nl)_0 = 0.016$.

For

$$\mathcal{L}^{-1}(r/nl) > 5,$$

$$\coth \mathcal{L}^{-1}(r/nl) = 1.0000$$

and

$$(r/nl) = 1 - 1/\mathcal{L}^{-1}(r/nl) \tag{6}$$

In terms of (r/nl) the range of validity for this approximation is $(r/nl) > 0.8$. In this range

$$\mathcal{L}^{-1}(r/nl) = 1/[1 - (r/nl)] \tag{7}$$

Then

$$E = \int_{0.016}^{(r/nl)>0.8} kTn\{1/[1 - (r/nl)]\}d(r/nl) \tag{8}$$

$$= \{ - kTn \ln[1 - (r/nl)]\}_{0.016}^{(r/nl)>0.8} \tag{9}$$

In comparison with the value of the integral at the upper limit of $(r/nl) > 0.8$ its value at the lower limit of 0.016 can be neglected. Therefore

$$E = - 2.303RTn \log [1 - (r/nl)], \ (r/nl) > 0.8 \tag{10}$$

per mole of macromolecular sections between entanglements, R being the gas constant. For $n = 2{,}700$ at 313° K

$$E = - 3900 \log [1 - (r/nl)] \longrightarrow \tag{11}$$

kcal/mole of macromolecular sections

A value of $(r/nl) = 0.9$ intuitively seems unreasonably high. Yet even for this value, E as calculated above is only about one one-hundredth of the observed degradation energy. In order for E to be equal to the observed degradation energy, values of $\log [1 - (r/nl)]$ around -100 would be required.

For purposes of discussion let us take 0.9 as the upper limit for the maximum acceptable value for (r/nl). Then about 100 macromolecular sections between entanglements would be required to store the observed degradation energy. Since the molecular weight of a macromolecular section between entanglements is about 150,000 there would be about 10 of these sections per molecule at the lowest molecular weight (1,500,000) for which degradation occurs for polyisobutene fractions[2].

It is improbable that these fractions contain any individual macromolecules ten times as big as the average. This is especially true for fractions precipitated from previously degraded polymer. Accordingly we must eliminate the activation of shear degradation by intramolecular energy concentration. Intermolecular concentration must be involved.

Storage completely as potential energy in bonds.—The maximum amount of energy that can be stored as potential energy in a bond is the activation energy for rupture (say 80 kcal/mole), since more than this would rupture the bond. If it is assumed that all this energy is dissipated upon rupture without contributing to overcoming viscoelastic resistance to flow, there can be calculated the minimum number of bonds that were involved in concentrating energy into the ruptured bond. The present results give a value in the neighborhood of 4,000 for this limit. A polyisobutene molecule of molecular weight 112,000 would have 4,000 chain bonds, so *at this limit* the possibility of intramolecular as distinct from intermolecular energy concentration is admitted. This lower limit, however, is probably much smaller than that corresponding to the true situation.

A higher estimate, though still not an upper limit, of the number of bonds involved in concentrating energy into the ruptured bond is obtained by considering the volume in the capillary shear field in which the energy used up per rupture is dissipated on a uniform basis. A representative figure for this energy, from Table I, is $320{,}000/6.2 \times 10^{23} = 5.31 \times 10^{-19}$ kcal per ruptured bond. Forty pounds may be taken as a representative part of the shear load corresponding to degradation energy. Following the calculation in the last

paragraph of the preceding section, in one shearing pass 5.31×10^{-19} kcal of degradation energy will be dissipated in a volume of $(5.31 \times 10^{-19} \times 1.307)/(40 \times 8.12 \times 10^{-6}) = 2.14 \times 10^{-15}$ cm³. In a 10 wt % solution of polyisobutene (density about 0.9 g/cm³) in *n*-hexadecane (density = 0.77 g/cm³) this volume corresponds to 3.6×10^6 chain atoms. A single polymer molecule incorporating all these atoms would have a molecular weight of 9.36×10^7, which is about 100 times higher than the values around 10^6 with which we are dealing here. Also a single molecule incorporating this many chain atoms would undoubtedly extend into a much larger volume than that stated above, sharing it with atoms from other individual molecules. Therefore by this estimate it seems necessary to rule out intramolecular energy concentration in favor of intermolecular energy concentration.

Combined effect of storage as deformation entropy and as potential energy.— The observed degradation energy is probably divided between reduced configurational entropy of deformation of molecular chains and potential energy in strained bonds. This division should not affect the conclusion of the two preceding subsections. They indicated that intermolecular concentration of energy is necessary to activate a macromolecular chain bond for rupture in mechanical shear degradation. This conclusion remains intact because the storage of free energy in a sequence of bonds forming a macromolecular chain or portion thereof as reduced configurational entropy and that as potential energy are not independent.

Consider a macromolecular chain changing from a configuration of greater probability to one of lower probability. The potential energy in the bonds involved will be greatest during the time the change is actually in progress. At this time there will be less than the final reduction of configurational entropy. However, when the change of configuration is completed the potential energy in the bonds will be at a minimum. The reduction of configurational entropy will also then be fully developed. Thus a given sequence of bonds cannot be involved at one time in both the maximum increase of potential energy and the maximum reduction of configurational entropy. When the increase of potential energy is large the reduction of configurational entropy is small and vice versa. If the two are mixed in substantial proportions of both it is not likely that the stored free energy associated with their sum will be appreciably greater than the maximum stored free energy associated with either one if it were present to the exclusion of the other.

CONCLUSION

The very large amount of energy consumed by the mechanical shear degradation process per mole of ruptured bonds can be readily explained within the framework of the mechanism propsed for this degradation process. This mechanism involves the activation of rupture in an individual bond by concentrating into it free energy introduced by the shear field into many other bonds or macromolecular chains and stored there. This concentrating of energy may be accomplished through any of several types of interatomic connections.

The observed values of the degradation energy indicate that intermolecular concentration of energy is necessary to accumulate sufficient energy into a macromolecular chain bond to activate its rupture. This conclusion is arrived at by quantitative estimates for two extreme cases of free energy storage during flow exclusively by: (1) reduced configurational entropy of deformation of

macromolecular chains and (2) potential energy of strained bonds in the macromolecular chains. In the second case one poor method of approximation permits intramolecular concentration of energy. This method is rejected in favor of a more realistic one requiring intermolecular concentration. The division of the observed degradation energy between the above two storage mechanisms is not likely to alter the conclusion requiring intermolecular concentration of energy for activation of rupture in mechanical shear degradation.

The variations of degradation energy with experimental variables apparently represent variations in the respective amounts of the stored free energy which does and does not contribute to overcoming viscoelastic resistance to flow after a bond ruptures.

SUMMARY

Molecular weight decrease by mechanical shearing results when solutions of around 10% of polyisobutene having average molecular weights above 500,000 are forced through a capillary at nominal rates of shear above 10,000 sec^{-1}. Comparison of observed plots of shear load vs. duration of shearing at fixed rates of shear during this degradation process with the corresponding estimated plots which would be expected to obtain if degradation did not occur provide a means of evaluating the amount of applied shearing energy which is dissipated by the degradation process. The result is several hundred thousand kilocalories per mole of broken bonds, which is several thousand times the bond energy of carbon-carbon bonds. This finding is consistent with the hypothesis that whenever a bond breaks the system loses much of the free energy temporarily stored in bonds and macromolecular chains located in a comparatively large volume surrounding the broken bond, these bonds and chains having been involved in concentrating the required activation energy into the ruptured bond.

ACKNOWLEDGMENTS

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STRENGTH AND ELASTOMERIC PROPERTIES OF RUBBER SOLUTIONS AND THEIR VULCANIZATES AT HIGH DEFORMATION RATES*

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Investigations of the strength and elastic properties of rubber solutions[1] and of vulcanizates are of interest in relation to studies of the formation and character of the structures in such solutions. We carried out determinations with the aid of an elastoviscometer for oscillographic recording of $P(\epsilon)$ curves at high values of $\dot{\epsilon}$[2], and also an elastorelaxometer[3] designed for direct measurements of elastic deformations in flowing systems at high values of $\dot{\epsilon}$. $P(\epsilon)$ curves for 6% solution of rubber in decalin are given in Figure 1.

It was found that, in agreement with earlier findings[1], the $P(\epsilon)$ curves for solutions of rubber (pale crepe) in decalin at 4, 6, and 10% concentrations, in

Fig. 1.—P (ϵ) curves for different values of $\dot{\epsilon}$ (numbers on the curves) for 6% solution of rubber in decalin.

the range $\dot{\epsilon}$ from 14 to 5000 sec^{-1}, pass through a maximum $P = P_r$, the position of which along the ϵ axis shifts with increasing $\dot{\epsilon}$ in the direction of increasing ϵ_r, reaching 5000% at high values of $\dot{\epsilon}$. The $\epsilon_r(\dot{\epsilon})$ relationship is linear.

Measurements of the elastic deformation by means of the elastorelaxometer for $\dot{\epsilon} = 143$ and 1142 sec^{-1} at $c = 4\%$ showed that the $\epsilon_e(\epsilon)$ curves also pass through a maximum, but this lies at $\epsilon_m \gg \epsilon_r$. The highest values of ϵ_e are 770 and 1100%.

Vulcanization of 2% rubber solution with 10% of S_2Cl_2 (on the weight of the rubber) sharply increases the relaxation time of the system. Therefore at $\dot{\epsilon} = 286$ sec^{-1} and total fixed $\epsilon = 5400\%$, the elastic deformation ϵ_e may reach 4000–5000% (1–2 days after the start of vulcanization of the solution (Figure 2). These results show that the chain regions between the junctions of the network may be deformed to 40 to 50 times their own length.

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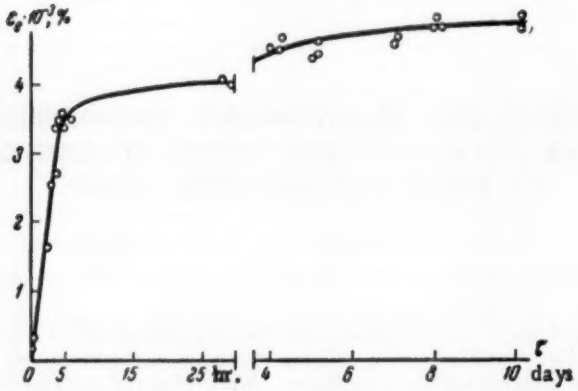

FIG. 2.—Time variation of the elastic deformation of 2% solution of rubber in decalin after addition of 10% S_2Cl_2 (fixed $\epsilon = 5400\%$; $\dot{\epsilon} = 286$ sec^{-1}).

The discrepancies between the positions of ϵ_r and ϵ_m on the $P(\epsilon)$ and $\epsilon_e(\epsilon)$ curves, and the shift of P_r in the direction of higher ϵ_r with increase of $\dot{\epsilon}$ show that the deformation and strength characteristics of rubber solutions are determined by a range of bonds in the system, characterized[3] by different ϵ_{ki} and ϑ_1. Therefore with increase of $\dot{\epsilon}$ the strength maximum is transferred to longer bonds, which relax at a higher rate.

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THE MECHANOCHEMICAL MODIFICATION OF HIGH POLYMERS *

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INTRODUCTION

Degradation of natural rubber during mastication has been shown to proceed *via* two alternative mechanisms[1], oxidative scission at high temperatures and mechanical scission at lower temperatures. The low temperature process, cold mastication, has received the greater attention[1–9]. The energy supplied to the extended rubber chains during mechanical deformation is sufficient to cause homolytic scission into polymeric free radicals[1,9]. The degradation of high polymers by a rupture process *via* mechanical scission has been shown to occur during the cold mastication of synthetic elastomers[4] and during the mechanical working of high molecular weight vinyl and acrylic polymers in the visco-elastic state[7,8]. The application of shearing forces to certain polymers in the brittle glass state[10] has provided evidence for both homolytic scission into polymeric free radicals and heterolytic scission into polymeric ions.

Polymeric radicals, produced by mechanical chain scission, have been used as initiators of vinyl polymerization to give block copolymers of an essentially linear character. Thus the block copolymerizations of methyl methacrylate, styrene, vinyl acetate, acrylonitrile, and ethyl acrylate have been initiated by mechanically shearing natural rubber, polymethyl methacrylate, polystyrene, polyvinyl acetate, polyethylene, polyvinyl chloride and polyvinyl formal during the process of extrusion[5,6] of the polymer plasticized to a viscoelastic state with the monomer. Many other polymer-monomer systems have yielded block copolymers by cold mastication[6].

Cold mastication of elastomer blends, such as natural rubber and neoprene, also leads to block copolymer formation by both combinative and hydrogen abstractive processes between the different species of elastomer radicals present[4]. If two polymers are completely compatible so that one continuous phase is present in the blend, and if the polymeric constituents have a common viscoelastic temperature range, then mechanical working during extrusion or internal mixing can lead to block copolymer formation. If the tendency of the polymeric radicals formed by mechanical rupture is to recombine rather than to disproportionate, then the chances of block copolymer formation are increased. The presence of sites for hydrogen or halogen abstraction upon one of the polymer constituents is also an aid to grafted block copolymer formation. Thus polyvinyl chloride-neoprene blends give grafted block copolymers on extrusion or internal mixing[11] and polyethylene-polyvinyl acetate blends block copolymerize when masticated in the absence of oxygen. Block copolymerization is largely controlled by the viscoelastic properties of the systems chosen.

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Natural rubber, unlike many of its synthetic counterparts, does not "gel" when masticated either in the presence or in the absence of oxygen[12]. Chain termination on scission is primarily de-activation by reaction with oxygen or free radical acceptors present in the nonrubber constituents. Evidence[12] has been presented, however, for chain branching by polymer transfer during the prolonged mastication of high molecular weight, acetone-extracted, deproteinized, pale crepe rubber. The mastication of rubber under nitrogen with suitable multifunctional reagents of the general structure MX_n, where M is an element of valency n in excess of 2, and X is a reactive group, should lead to the formation of crosslinked gelled structures. Several classes of structurally different reagents have been found to be capable of reacting in this way. One such class includes the aluminium alkoxides which have been studied extensively as gelling agents for natural rubber[13]. As little as 0.1 per cent of aluminium isopropoxide when masticated with acetone-extracted pale crepe for from 1 to 5 minutes, gives more than 90 per cent of gel insoluble in benzene. The mechanochemical gelation of synthetic elastomers, e.g., neoprene and hyperlon, is similarly accelerated by the presence of aluminium alkoxides[15].

Since the gelation reaction is a mechanochemical process independent of the chemical structure of the elastomer, the reaction should be applicable to nonrubbers, i.e. plastomers, masticated while in a viscoelastic state. This has been found to be the case for polymethyl methacrylate, polyvinyl acetate and polyethylene. No evidence for the crosslinking of polystyrene, however, has been obtained.

By masticating blends of polyethylene and polyvinyl acetate, block copolymerization can be achieved, provided oxygen is rigidly excluded and the mastication is carried out for prolonged periods. By the addition of aluminium isopropoxide higher proportions of block copolymeric materials are formed under less rigid conditions of oxygen exclusion and in shorter periods of mastication.

EXPERIMENTAL

Materials.—All polymers were commercial products, polymethyl methacrylate (*Perspex* of I.C.I. Ltd), polystyrene (supplied by Distillers Company Ltd), polyvinyl acetate (*Gelva* 2.5, Shawinigan Ltd), polyethylene (*Alkathene* 2, I.C.I. Ltd), and were used without purification or fractionation. Aluminum isopropoxide (Honeywill and Stein Ltd) of purity greater than 95 percent was used as the gelling agent.

Mastication.—The masticator used for obtaining experimental data was a standard production model of the BRPRA. laboratory one-rotor mixer[14], manufactured by Baker Perkins Ltd. Plow scroll attachments rotating at a speed of 40 rpm were used throughout and no precautions, apart from totally filling the mastication chamber, were taken to exclude atmospheric oxygen except where stated. The mastication procedure and the manipulation of polymer-additive and polymer-polymer mixtures have been described previously[2–9]. In the following experiments the required quantity of alkoxide was added to the polymer in the mastication chamber, thorough mixing being achieved during the first minutes of mastication in the viscoelastic state. After consecutive periods of mastication approximately 0.25 g samples were removed from the chamber and their gel contents determined. In this way the course of reaction was followed without materially altering the conditions of mechanical shear. The chamber volume was adjusted after each period of mastication to allow for the material removed.

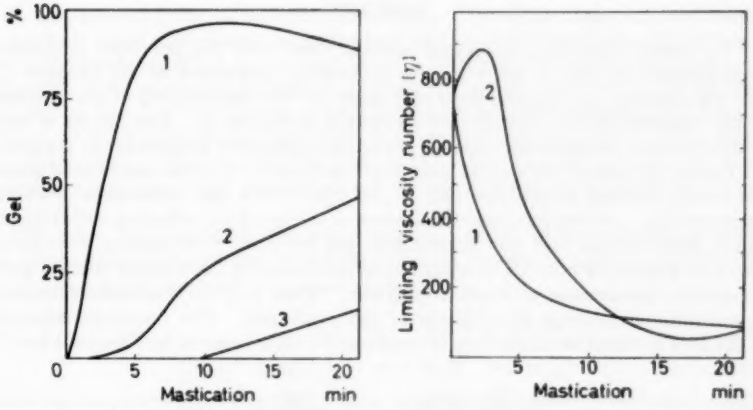


FIG. 1.—Mastication of plastomers with 0.5 per cent aluminum isopropoxide: 1, polymethyl methacrylate at 140° C; 2, polyvinyl acetate at 90° C; 3, polyethylene at 90° C.

FIG. 2.—Mastication of polymethyl methacrylate with 0.5 per cent aluminum isopropoxide: 1, in air at 140° C; 2, in air at 140° C with 0.5 per cent aluminum isopropoxide (sol fraction).

Gel content and swelling index.—The 0.25 g samples were weighed into tared glass thimbles which were contained in weighing bottles to which the appropriate solvent (25 ml) was added. The gel contents were calculated from determinations of the sol concentration. The thimbles were drained from excess solvent and reweighed. By drying down under vacuum and correcting for the sol content of the swelling liquid, the swelling index (grams of solvent per gram of polymer) was obtained in each instance.

Viscometric determinations.—Limiting viscosities of the sol fractions in benzene solution were determined by conventional means. The relationship $M_n = 2.81 \times 10^5[\eta]^{1.32}$ was employed to give values of the number-average molecular weight for the unfractionated polymethyl methacrylate sols.

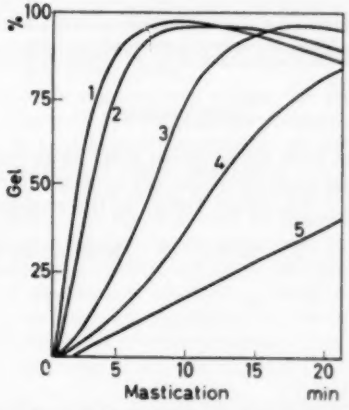
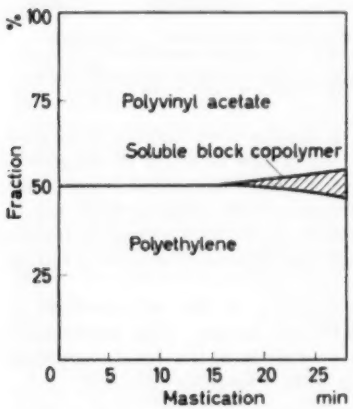


FIG. 3.—Effect of aluminum isopropoxide concentration on the rate of gelation: 1, 1.0 per cent aluminum isopropoxide, in air; 2, 0.5 per cent, in air; 3, 0.1 per cent, in air; 4, 1.0 per cent, under oxygen; 5, 1.0 per cent aluminum isopropoxide +0.5 per cent thio-2-naphthol.

RESULTS

The mastication of polymethyl methacrylate with 0.5 per cent aluminum isopropoxide at 140° C gave rise to increasing quantities of gel (Figure 1). The viscosities of the sol fractions and those for the degradation of the polymer in the absence of the alkoxide are compared in Figure 2. The effects of concentration and mastication time for the same system are illustrated in Figure 3.

Blends of polyethylene and polyvinyl acetate (1:1) were masticated under the same physical conditions (95° C, 40 rpm) with and without aluminium isopropoxide. Separation into fractions was obtained by refluxing with toluene which dissolved all but any crosslinked gel fraction. On cooling, free polyethylene separated out. The addition of methanol to the toluene filtrate gave a granular precipitate of black copolymer. Free polyvinyl acetate remained in the toluene solution on addition of the methanol. The fractional analysis of the two systems as a function of mastication time is given in Figures 4 and 5.



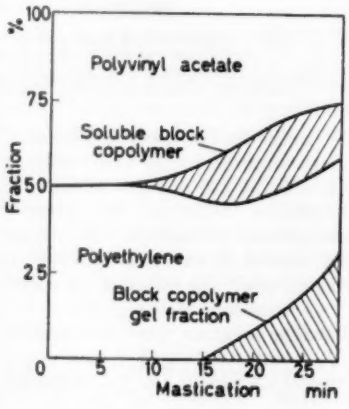


FIG. 4.—Fractional analysis of blends of polyvinyl acetate and polyethylene after mastication under nitrogen at 95° C. Chamber completely filled by polymer blend.

FIG. 5.—Fractional analysis of blends of polyvinyl acetate and polyethylene after mastication in air with 0.5 per cent aluminum isopropoxide at 95° C. Chamber incompletely filled.

DISCUSSION

The aluminum atom from the alkoxide must be an essential part of the gel structure, since chemical analysis of the ash from gel fractions gave more than 95 per cent of alumina. The exact nature of the crosslinks, whether they are

$$\cdot\mathrm{Al}\cdot, \quad \cdot\mathrm{O}\cdot\mathrm{Al}(\mathrm{O})\cdot\mathrm{O}\cdot, \quad \text{or} \quad \cdot\mathrm{R}\cdot\mathrm{O}\cdot\mathrm{Al}(\mathrm{O}\cdot\mathrm{R})\cdot\mathrm{O}\cdot\mathrm{R}\cdot$$

cannot easily be determined. The degree of gel formation and the gel swelling (which is determined by the chain length between crosslinks) are dependent

upon the concentration of alkoxide (Figure 3). The dependence of the degree of gelation upon the molecular weight of the polymer, and the "retarding" effect of thio-2-naphthol are indicative of a free radical mechanism which is initiated by the mechanical scission of polymer chains. From previous studies it is known that the mastication of bulk-polymerized polymethyl methacrylate is more efficient in inducing degradations than that of either polyvinyl acetate or polyethylene. The viscoelastic state of the latter two polymers is not conducive to producing high concentrations of free radicals by mechanical shear (Figure 1).

The initial increase in the limiting viscosity number of the sol fraction from the polymethyl methacrylate would suggest that the reaction proceeds through a branching mechanism of the general scheme:

$$R_x \cdot R_y \longrightarrow R_x \cdot^{*} + R_y \cdot^{*} \qquad \text{(i)}$$

$$R_x \cdot^{*} + AlR'_3 \longrightarrow R_xR \cdot + AlR'_2{}^{*} \qquad \text{(ii)}$$

$$AlR'_2{}^{*} + R_y \cdot^{*} \longrightarrow Al(R'_2)R_y \qquad \text{(iii)}$$

$$Al(R'_2)R_y + R_y \cdot^{*} \longrightarrow R_yR' + AlR'R_y{}^{*} \qquad \text{(iv)}$$

$$AlR'R_y{}^{*} + R_x \cdot^{*} \longrightarrow AlR'R_xR_y \qquad \text{(v)}$$

$$AlR'R_xR_y' \longrightarrow AlR_xR_yR_z \qquad \text{(vi)}$$

where R_x, R_y, and R_z represent segments of polymer chains. Further scission of these combined polymer chains, coupled with reaction with alkoxide or substituted alkoxide residues, leads to the formation of gel fractions. Initially such branched structures as are formed in the suggested reactions (i) to (vi) could lead to chain lengthening since the combined polymer chains are statistically more likely to have come from the higher molecular weight molecules (more susceptible to mechanical rupture). Continued scission rapidly reduces the average viscometric molecular weight of the sol fraction which finally falls below the limiting value normally achieved for the mastication of the polymer in the absence of alkoxide. This lower value for the sol fraction occurs because the majority of the sheared polymer chains are incorporated into the gel fraction. The upturn which occurs after comparatively long periods of mastication can be attributed to the soluble products from the mechanical degradation of the gel fraction, a result of over mastication.

Although the viscoelastic temperature ranges for polyethylene and polyvinyl acetate overlap, relatively few radicals are produced by shear in mastication (Figures 1 and 4) so that long mastication in the absence of oxygen is required to synthesize appreciable block copolymer fractions. Thus mastication under nitrogen of a 1:1 blend at 95° C gave 7 per cent of block copolymer after 30 min. The addition of 0.5 per cent of aluminium isopropoxide increased the block copolymer fraction in the same time to 15 per cent. In this latter instance mastication was carried out in air and there was approximately 3 ml of air space in the mastication chamber. Under such conditions in the absence of the alkoxide no block copolymerization was achieved. Fragments of each of the degraded polymers were incorporated into the sol and gel block copolymer fractions by reactions of the general type:

$$P \cdot P + AlR'_3 \longrightarrow PR' + P \cdot AlR'_2 \qquad \text{(vii)}$$

$$P \cdot AlR'_2 + R \cdot R \longrightarrow RR' + P \cdot Al(R') \cdot R \qquad \text{(viii)}$$

where P represents a polyethylene chain, and R a polyvinyl acetate chain, and R′ the alkoxy group. Chemical analysis of the ash from the block copolymer fractions established the presence of alumina. The presence of polyvinyl acetate in the sol and gel block copolymer fractions was established by hydrolysis (refluxing with a 1:1:1 mixture of sulfuric acid, methanol and water). The block copolymer fractions resembled polyethylene in appearance, the gel fraction being harder and the sol fraction softer than the initial polyethylene. Thus both soluble and crosslinked block copolymeric products were synthesized by the addition of minor quantities of aluminum isopropoxide to the polymer blends before mastication.

In the foregoing suggested reaction mechanisms (i) to (viii) the symbol R* has been used to denote the active polymer fragments produced by mechanical scission of the polymer chains. If the scission is homolytic the reactions will be freeradical in nature, but if the scission is heterolytic, producing polymeric ions, ionic mechanisms will operate. Current investigations indicate that heterolytic scission can take place under the operating conditions in which these experiments were carried out[16]. The exact nature of the polymer fragments, and the detailed mechanism of the reactions have not, therefore, been specified since it is possible that both types of reaction are occurring simultaneously.

SYNOPSIS

The mechanical degradation of high polymers by shearing forces has been shown to occur by homolytic and by heterolytic scission. Heterolytic degradation into polymeric free radicals during the mastication of both rubbers and plastomers has been used to synthesize block copolymers. The mastication of high polymers in the presence of multifunctional reagents such as aluminum isopropoxide leads to the formation of crosslinked gel structures. By subjecting suitable blends of two or more polymers to mechanical degradation in the presence of an alkoxide, soluble and crosslinked block copolymers can be synthesized. These reactions are discussed in terms of free radical and ionic mechanisms.

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MECHANOCHEMICAL REACTIONS LEADING TO REINFORCEMENT IN RUBBERS *

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The development of the single rotor internal mixer[1] (at the British Rubber Producers' Research Association) has facilitated the research into mechanochemical reactions of a wide range of high polymers. The term "mechanochemical" has been applied to reactions such as mastication, the mechanism of which involves the primary step of mechanical scission of a polymer chain into polymeric free radicals at a carbon to carbon or other covalent bond. The processes which have been studied previously include the cold mastication of rubberlike polymers[2–4], the formation of carbon gel[5,6], the interpolymerization of two elastomers during blending[7], and block copolymerization by the cold mastication of polymers plasticized by vinyl monomers[8–11]. The evidence for the polymeric free radical nature of these reactions has recently been reviewed[12]. The reactions can be summarized as follows:

Scission	$R{-}R$	$\longrightarrow R\cdot + R\cdot$			(1)
Recombination	$R\cdot + R\cdot$	$\longrightarrow R{-}R$			(2)
Peroxy radical	$R\cdot + O_2$	$\longrightarrow RO_2\cdot$	$\longrightarrow$ stable products		(3)
Radical acceptor	$R\cdot + HS.Ph$	$\longrightarrow RH + Ph.S\cdot$	$\longrightarrow (Ph.S)_2$		(4)
Carbon gel	$R\cdot + :\!\bullet\cdot$	$\longrightarrow R{-}\bullet\!\cdot$	$\longrightarrow R{-}\bullet\!<^{R}_{R}$		(5)
Blending (i)	$R{-}R + S{-}S$	$\longrightarrow 2R\cdot + 2S\cdot$			(6)
(ii)	$R\cdot + S_S$	$\longrightarrow R{-}S_S$	$\longrightarrow$ gel		(7)
(iii)	$S\cdot + R_R$	$\longrightarrow S{-}R_R$	$\longrightarrow$ gel		(8)
Interpolymerization	$R\cdot + S\cdot$	$\longrightarrow R{-}S$			(9)
Block copolymer	$R\cdot + nM$	$\longrightarrow RM_n\cdot$	$\longrightarrow RM_n$		(10)

The apparent rate of mechano degradation of natural rubber is greatly reduced in the absence of radical acceptors. This is due to the recombination of the rubber free radicals which is a competitive reaction[2]. Oxygen and some of the nonrubber constituents of natural rubber (the short stops and antioxidants in the case of synthetic rubbers) are efficient radical acceptors and it is therefore necessary to carry out Reactions 5 to 10 under nitrogen with acetone-extracted rubbers to achieve the maximum of interaction. Since the reactions

* Reprinted from the *Proceedings International Rubber Conference*, Washington, D. C., November, 1959, pages 410–416.

are competitive, the rigid exclusion of oxygen and the complete extraction of nonrubber constituents are not essential when very high molecular weight rubbers are subjected to high rates of mechanical shear and when only a limited extent of reaction is required. Unlike the previously reported mechanochemical reactions[12], those described here are not directly affected by the presence of oxygen or other radical acceptors. In addition, they give rise to a measure of reinforcement in unfilled gum stocks.

The cold mastication of natural rubber with compounds with the general formula MX_n—e.g., $SnCl_4$, $FeBr_3$, $Al(OH)_3$ (where M is a metal with a valency greater than 2 and X is a halide, hydroxide, or nitrate—leads to the formation of an insoluble gel fraction. The majority of these polar compounds were hygroscopic and the presence of hydrated material was found to reduce the efficiency of gelatin. Attention was therefore turned to the aluminum alkoxides, a class of compounds which are equally reactive as gelling agents but which are not appreciably hydrolyzed in air. They also have the advantage of complete compatibility with the majority of rubbers and rubberlike polymers over a wide range of concentrations.

EXPERIMENTAL METHODS AND PROCEDURES

Gelling agents.—The majority of experiments were carried out with aluminum isopropoxide and aluminum *sec*-butoxide because these alkoxides were commercially available (Honeywell and Stein, Ltd.). They were used without purification and kept over fused calcium chloride. Aluminum *tert*-amyl oxide was prepared according to the method of Teichner[13] from redistilled *tert*-amyl alcohol and resublimed aluminum chloride. Metal halides and alumina were of Analar grade, while the activated alumina was a commercial flake variety ground to 240 mesh. Aluminum hydroxide was prepared from aluminum isopropoxide by hydrolysis in benzene solution with aqueous refluxing acetone.

Rubber.—Thin sheets of pale crepe with an initial Wallace plasticity of 63 (Mooney number 27) and having a nitrogen content of $< 0.1\%$ and an oxygen content of 0.7% were used without homogenization by milling so as to retain the high molecular weight (limiting viscosity number in benzene $[\eta] = 5.7$). Chemical analysis, solution viscosity, and Wallace plasticity measurements on samples from different portions of the same batch of pale crepe showed variations within the limits of experimental error only. For the experiments with "extracted rubber" the pale crepe was Soxhlet-extracted with acetone for 24 hours and stored under vacuum until required for use.

Experimental methods.—The gelation experiments were carried out in the 2-inch single rotor internal mixer[1] using the plough type of scrolls rotated at 120 rpm. Additional experiments were carried out on a David Bridge 12×6 inch two-speed mixing mill in a 2-inch David Bridge extruder.

The percentage gel in masticated sample and the degree of swelling of the gel fractions were determined by allowing 0.1 gram of the rubber, contained in a glass thimble with a coarse sintered base, to reach equilibrium while immersed in 10 ml of Analar benzene. The thimble, rubber, and benzene were contained in 2×1 inch glass weighing bottles which were maintained at room temperature in the dark for 6 days before measurements were carried out. Gel contents were obtained by difference by determining the concentration of rubber in 2.5-ml aliquots of the centrifuged sol fraction. The gel swelling indexes (grams of benzene per gram of rubber gel) were calculated from the weight in situ of the swollen rubber in the thimble after removing nonabsorbed benzene

from the gel surface and from the glass thimble with filter paper. Corrections for the sol fraction in the gels were made.

Six-gram portions of the rubber together with the appropriate weight of additive were masticated for 5 seconds before flushing out the masticator with nitrogen. This procedure was adopted to minimize the loss of finely powdered additives during the flushing out process. After the appropriate period of mastication with a chamber volume of 6.5 ml, the rubber was removed from the chamber and approximately 0.1 gram of the rubber was retained for gel content measurement. The bulk of the rubber was then returned to the masticator and mastication continued for further periods of time, 0.1-gram samples being removed between masticators. Circulating water, at 12° to 15° C (higher temperatures where indicated), was passed through the masticator scrolls in all experiments.

Since the experiments with the small masticator indicated a very fast reaction under conditions of maximum shear, sheets of pale crepe were dusted

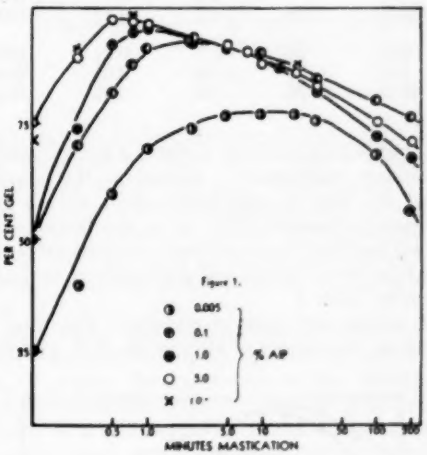


FIG. 1.

with the powdered alkoxide and passed through the tightest nip obtainable with full water cooling on the two rolls (12° C) for the milling experiments. Similarly, for extrusion, strips of pale crepe were dusted with the powdered alkoxide and then fed into the extruder. A 2-cm-diameter die was used with water cooling along the barrel and the die head heated to 80° C.

RESULTS

Variation of gel content with extent of mastication.—The rate of reaction of 0.1% of aluminum isopropoxide with acetone-extracted rubber was extremely rapid under the conditions of high mechanical shear which were achieved in the laboratory masticator. Within 15 seconds of the commencement of the mastication 70% of the rubber was gelled. A maximum in the gel content was achieved after 1 minute's mastication; thereafter the gel content decreased. Increasing the percentage of isopropoxide to 5% gave an even greater rate of

TABLE I

GEL CONTENT AND DISTRIBUTION OF COMBINED ALUMINUM ISOPROPOXIDE

Alkoxide, %	Min. mastication	Gel, %	Gel, swelling	Alkoxide in gel, %	Alkoxide in sol, %	Unreacted alkoxide
10.0	0.75	98	13	1.7	—	8.3
	5.0	93	11	1.8	2.1	8.2
	40.0	80	8	2.0	2.0	8.0
5.0	0.75	97	15	1.5	—	3.6
	5.0	92	13	1.7	0.5	3.4
	40.0	82	12	1.8	1.3	3.3
1.0	0.75	92	23	1.0	0.9	0.1
	5.0	90	18	1.0	1.0	0.0
	40.0	78	15	1.1	0.7	0.0
0.1	0.75	86	25	0.10	0.10	0.0
	5.0	90	21	0.11	0.09	0.0
	40.0	84	17	0.13	0.08	0.0
0.005	0.75	66	31	0.01	0.0	0.0
	5.0	77	25	0.01	0.0	0.0
	40.0	76	23	0.01	0.0	0.0

gelation (Figure 1), but with as little as 0.005% a considerable gel content was reached after 20 minutes' mastication. Increasing the quantity of aluminum isopropoxide beyond 5% had no significant effect on the gel content or gel swelling. The unreacted alkoxide dissolved in the benzene and was removed from the recovered sol fractions by subsequent acetone extraction. The distribution of the alkoxide between the sol and gel fractions, as determined by micro ash analysis, is given in Table I.

Variation of gel content with type of additive.—The most effective gelling agents were found to be the halides of aluminum, iron, and tin, but the repro-

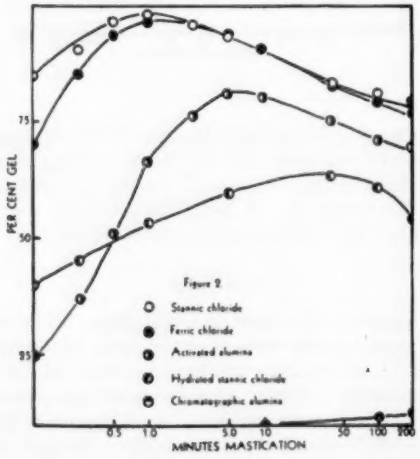


FIG. 2.

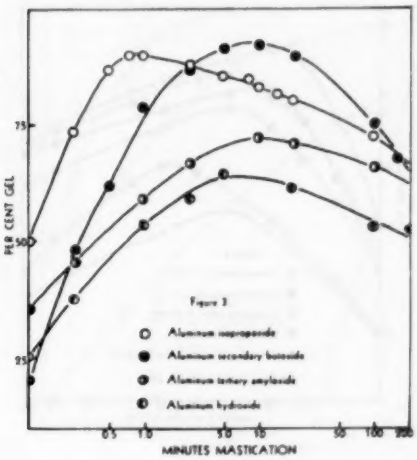


FIG. 3.

ducibility was poor because of the wetting of the scrolls by the products of hydrolysis due to absorbed moisture. The relative gelling efficiencies at a concentration of 1.0% of stannic chloride, ferric chloride, activated alumina, hydrated stannic chloride, and chromatographic alumina are reported in Figure 2. The efficiencies of the alkoxides as gelling agents decrease with the increase in chain length of the alkyl group (Figure 3), approaching that of the derived aluminum hydroxide. The highest gel contents were also associated with the lowest gel swellings (Table II).

Gel formation on milling with free radical acceptors.—Mastication in the presence of air had very little effect on the rate of gelation or the extent of gelation achieved. Likewise the extraction of the rubber with acetone had little effect on the course of the gelation reaction (Figure 4). The expected complete suppression of the gelation by thio-2-naphthol and 2,2-diphenyl-1-picrylhydrazyl was not found and there was little variation in gel content for different grades of natural rubber.

Variation of gel with temperature of mastication.—The gelation reaction has the negative temperature coefficient which is associated with reactions initiated by mechanical rupture of polymer chains (Figure 5). At the higher temperatures of mastication the rubber is more plastic and more easily deformed,

TABLE II

GEL CONTENT AND SWELLING AFTER 5 MINUTES' MASTICATION WITH 1% ADDITIVE

Additive	Gel, %	Gel, swelling index
Stannic chloride	95	7
Ferric chloride	93	13
Aluminum isopropoxide	90	18
Aluminum *sec*-butoxide	91	21
Activated alumina	81	25
Aluminum hydroxide	65	31

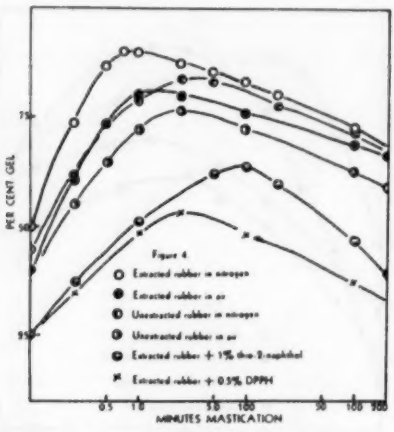


FIG. 4.

so that less mechanical energy is available for rupturing chemical bonds—i.e., the rate of shear is less. This has the over-all effects of slowing down both the rate of formation of the gel fraction and the rate of degradation of the gel fraction.

Gel formation with synthetic rubbers.—When neoprene was masticated alone in nitrogen gel, formation occurred after 25 minutes' mastication. In the presence of 1% of aluminum isopropoxide, however, gel was formed right from the start of mastication (Figure 6). Hypalon was similarly gelled under the same conditions. The mastication of butadiene-styrene, nitrile, and butyl rubbers with 1% of alkoxide for periods up to 10 minutes under nitrogen at 12° C did not result in the formation of any appreciable gel fractions.

Gel formation on a two-roll mill.—Unextracted pale crepe, dusted with 1% of aluminum isopropoxide, gave increasing gel contents when subjected to up

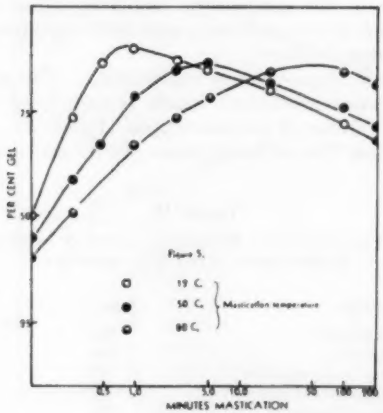


FIG. 5.

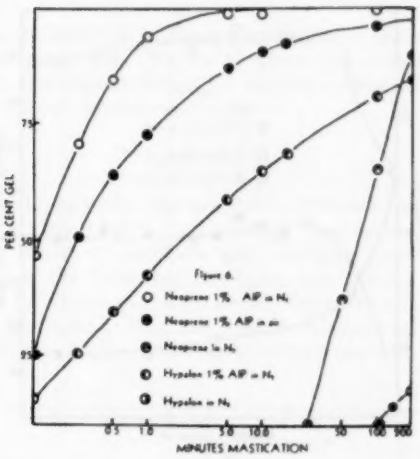


FIG. 6.

to 8 passes through a 0.005-inch nip of the two-roll mill with roll temperatures of 15° C, running at friction speeds. After 8 passes the gel content decreased (Figure 7). To evaluate the physical properties of these pregelled vulcanizates, 3% of dicumyl peroxide was added after 8 passes and banded in the normal way with a reduced nip (0.1 inch), and with the roll temperatures increased to 80° C to minimize the breakdown of the gel during compounding and to facilitate the dispersion of the dicumyl peroxide.

Gel formation in a 2-inch extruder.—One-inch strips of pale crepe dusted with 1% of aluminum isopropoxide were fed continuously into the extruder and the Wallace plasticity and gel content measured at 1-minute intervals on the

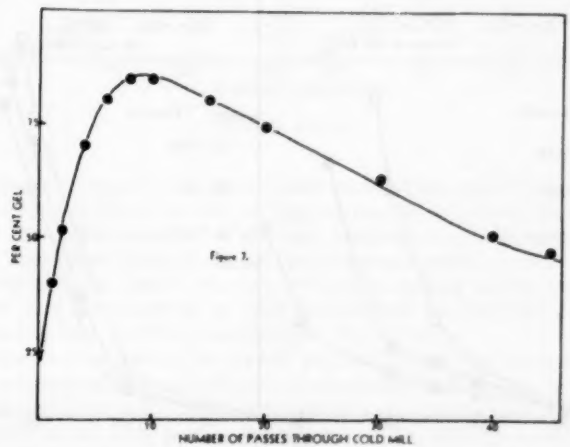


FIG. 7.

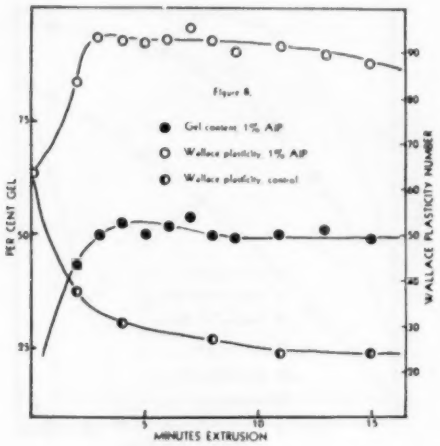
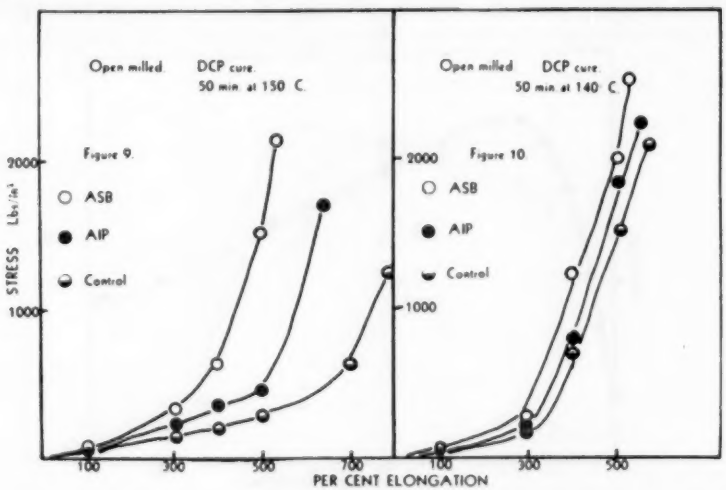


FIG. 8.

extruded rubber. Plasticity and gel content rose rapidly initially and then leveled off to more or less constant values as equilibrium shearing conditions were reached (Figure 8).

Stress strain measurements on pregelled vulcanizates.—Gum stocks gelled with 1% of aluminum isopropoxide and 1% of aluminum secondary butoxide were prepared and compounded with dicumyl peroxide as described. Vulcanization was carried out in multidaylight autocontrolled steam-heated presses. Control stocks were given the same milling, extruding, or masticating treatments and vulcanized under the same conditions. The tensile data for these two systems

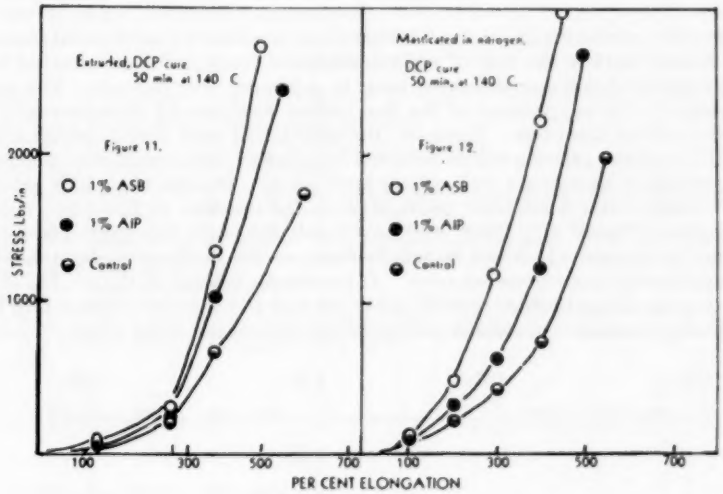


FIGS. 9 AND 10.

are compared with the controls in Figures 9 and 10 for the compounded stocks prepared on the two-roll mill. Figure 11 gives the comparable data for extruded compounds, and Figure 12 that for natural rubber internally masticated under nitrogen in the laboratory masticator.

DISCUSSION

The high gel contents which are achieved with such low concentrations of alkoxides (75% gel with 0.005% of aluminum isopropoxide after 5 minutes' mastication under nitrogen) preclude any postulate depending upon filler-particle interaction of the type that has been observed for carbon gel formation[5,6]. The rapid formation of the gel during the early stages of cold mastication (Figures 1 to 4), together with the negative temperature coefficient of the gelation reaction (Figure 5), does, however, indicate the shear-dependent nature



FIGS. 11 AND 12.

of the gel-forming reactions. It has been shown that under constant conditions of mechanical shear the rate of degradation to polymeric free radicals is greatest at the commencement of the cold mastication of high polymers[2]. It was found that when natural rubber was premasticated in air to reduce its molecular weight, the rate of reaction with these gelling agents was considerably reduced and the maximum gel content achieved was inversely proportional to the extent of the previous breakdown of the rubber.

The presence of aluminum in the ash from the gel and sol fractions was confirmed by microchemical analysis and this indicated that either the aluminum atom or the oxy-aluminum group was acting as a trifunctional cross-linking agent. Gels formed from higher concentrations of alkoxide contained more aluminum and swelled to a less extent than those formed at lower alkoxide concentrations (Table I). Since both stannic chloride and ferric chloride are

known cyclizing agents for natural rubber, the degree of unsaturation of the gel fractions was estimated by reaction with peracetic acid. In no case was the unsaturation below 96% of that for natural rubber, and the average value for the isopropoxide gels was 98.5%. Natural rubber solutions in benzene were degassed and refluxed under nitrogen with 2% of aluminum isopropoxide for 24 hours but no gelation occurred and the rubber after recovery and acetone extraction contained no aluminum as ash.

The physical and chemical evidence presented suggests an over-all reaction of the following type:

$$R{-}R \longrightarrow R{-} + R{-} \quad (1)$$

$$R{-} + Al(OR')_3 \longrightarrow RAl(OR')_2 \quad (2)$$

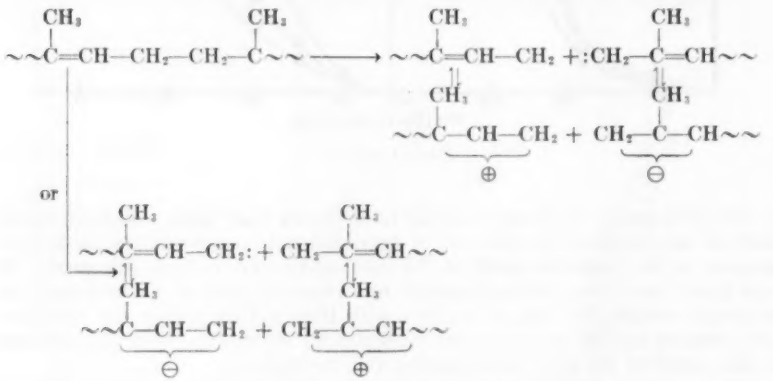
$$R{-} + RAl(OR')_2 \longrightarrow R_2Al(OR') \quad (3)$$

$$R{-} + R_2Al(OR') \longrightarrow R_3Al \quad (4)$$

$$R_3Al \longrightarrow R_2AlR'' + R{-} \longrightarrow \text{gel} \quad (5)$$

where R— represents an "active" rubber chain produced by mechanical scission.

Earlier work in the field of mechanochemical reactions[12] has indicated that the rupture of polymer molecules leads to polymeric free radicals. The main evidence is the suppression of the free radical reactions by deactivation with added radical acceptors. However, the addition of both thio-2-naphthol and DPPH to these gelation reactions failed to suppress them completely, contrary to prediction based on a free radical mechanism. Greater than 50% gel was still formed after 5 minutes' mastication in the presence of these free radical acceptors (Figure 4). Polar and ionic mechanisms are the only alternative forms of reaction which can be put forward, on the evidence so far available, to explain this anomalous behavior. If heterolytic scission of the $-CH_2-CH_2-$ bond in natural rubber were to occur (as well as homolytic scission into free radicals), resonance-stabilized polymeric ion structures could result:



Gelation reactions could thus be attributed to a polar mechanism by interaction of these polymeric carbanions and carbonium ions with the polarized or ionized alkoxide or halide. Further experimental work is in progress to determine the course of the gelation reaction and the influence of both free radicals and ions upon the mechanisms.

The physical properties of the vulcanizates prepared from the gelled rubbers indicate a measure of reinforcement, although no claim is made for having achieved the optimum curing conditions for the systems. A full evaluation is in progress[14]: Initial results indicate that gelled rubbers, natural and synthetic, prepared in this way can be added to gum stocks to improve processing behavior during extrusion, calendering, etc. These gelation experiments have been extended to plastomers mechanically shared while in a rubber state[15] and to other additives with widely differing chemical structures[16].

ACKNOWLEDGMENT

The author acknowledges the help of the British Rubber Producers' Research Association in permitting the use of the internal single rotor masticator for these experiments. This work forms part of the program of research which is being undertaken at the National College of Rubber Technology. The helpful discussions with F. H. Cotton, J. Glazer, and G. N. Welding, in the course of this reasearch are greatly appreciated.

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GEL FORMATION IN THE MASTICATION OF NATURAL RUBBER, AND ITS INFLUENCE ON VULCANIZATE STRENGTH *

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Angier and Watson observed formation of spatial structures (gels) in neoprene rubber[1], certain SBR fractions, and butadiene-acrylonitrile rubber[2], under the influence of powerful shearing forces during treatment in a specially designed scroll-type masticator[3]. This gel formation was considered to be a specific characteristic of synthetic rubbers; no one has reported gel formation in the mastication of natural rubber (NR). In our experiments an insoluble gel was formed in NR. Weighed samples of extracted smoked sheet were masticated in an argon atmosphere containing not more than 0.05% oxygen, on specially designed rolls[3], with 0.12 mm gap between the rolls cooled intensive with water.

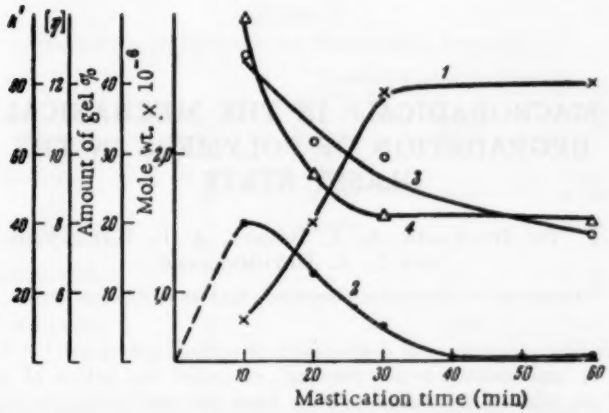
The formation of an insoluble fraction (gel) at the early stages of mastication was established in repeated experiments. Its maximum content (after 10 minutes of mastication) reaches 20%, and further milling results in mechanical dispersion of the gel fraction, so that after 60 minutes of mastication the rubber is again completely soluble in the common solvents. However, the masticated rubber contains formations branched to such an extent that most of them (~80%) are precipitated from octane solution by centrifugation at 12,000 rpm for an hour. Molecular weight determinations, based on changes in the light scattering of the solutions at an angle of 90°, showed that the molecular weights of the sol fractions of the masticated samples increase during mastication, reaching 2,500,000 after 60 minutes. The true molecular weight of the particles is apparently of major significance, as a correction for the asymmetry of the scattering particles was not applied.

Gel formation is not observed if the argon contains more than 0.1% of oxygen, which terminates the free radicals formed in the mechanical rupture of the molecular chains of the rubber.

In absence of oxygen, secondary reactions of the radicals lead to the formation of branched molecules, which are more compact particles offering less resistance to shearing deformations, and therefore the intrinsic viscosity (and hence the average molecular weight determined from the viscosity) decreases in the course of mastication. The slope of the η_{sp}/c curves, which is a measure of the Huggins constant k', decreases during mastication; this suggests that the structural fragments in microgel form are spherical, with a higher density of the rubber substance in the molecular coil.

A very important fact is that the presence of branched formations (microgel) in natural rubber masticated under the conditions described lowers the tensile strength of unfilled sulfur vulcanizates to 20–40 kg/cm², i.e., to values typical

* Reprinted from *Colloid Journal* **20**, 629 and 630 (1958); a translation by Consultants Bureau Enterprises, Inc. of *Kolloid. Zhur.* **20**, 674 and 675 (1958).



Molecular changes in natural rubber during mastication in argon: (*1*) Molecular weight by light scattering; (*2*) amount of gel; (*3*) intrinsic viscosity; (*4*) Huggins constant.

for unfilled vulcanizates of noncrystallizing synthetic rubbers. It is known that the strength of vulcanizates of natural rubber, masticated normally in presence of air, reaches 200–250 kg/cm². Thus, the mechanical strength of rubber vulcanizates depends not only on the molecular structure, which is determined by the composition, relative positions, and sequence of the atomic groups, but also on the degree of branching[5] of the molecules, and in particular on the presence of microgel in the rubber.

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MACRORADICALS IN THE MECHANICAL DEGRADATION OF POLYMERS IN THE GLASSY STATE *

P. Yu. Butyagin, A. A. Berlin, A. E. Kalmanson and L. A. Blyumenfeld

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The radical mechanism of degradation of organic polymers[1, 2, 5, 6, 7] during grinding or mastication, or on freezing[3], or under the action of ultrasonic waves[4, 8] in solution has until recently been demonstrated only by indirect methods. These make it possible to postulate the formation of polymer radicals involving the influence of acceptors upon the rate and limit of degradation, the initiation of polymerization of monomers and the formation of block or graft copolymers. The question of the formation of polymeric radicals and macro-ionic structures in mechanical degradation of inorganic and elemental organic polymers has been considered from theoretical standpoints[1, 7, 8] but up to recent times[11] has not been experimentally confirmed even by indirect methods. At the same time a necessity for a direct confirmation of the formation of macroradicals in various mechanical actions upon polymers is of fundamental importance both as a basis of the mechanism of mechanochemical conversions of macromolecules and for establishing the influence of various factors upon the life, chemical conversions and block-graft copolymerization of macroradicals. In the study reported here we employed electron paramagnetic resonance (EPR) spectra. The EPR spectra were measured on a radiospectrometer with double magnetic modulation, built according to Semenov and Bubnov[12]. In the spectrometer we employed high-frequency modulation of the magnetic field at a frequency of 975 kc/s with an amplitude less than the width of the line, and low-frequency field sweep. As a result the line is recorded in the form of the first derivative of the absorption curve. The sensitivity of the apparatus was 3×10^{12} paramagnetic particles (calibrated with diphenyl picryl hydrazyl at room temperature). Quantitative measurements of the concentration of paramagnetic particles in the specimens were carried out by means of comparison with the spectrum of a standard specimen of diphenyl picryl hydrazyl. The width of line for singlet signals is expressed in distances between the points of maximum slope and is designated as ΔH. For measurement at low temperature we used a foamed plastic vessel, filled with liquid nitrogen and placed directly in the resonator. As well as the EPR spectra we determined the specific surface of the specimens (low temperature absorption of argon, Brunauer-Emmett-Teller, "BET" method) and the mean viscosity molecular weight of the polymers.

The materials under investigation were mechanically degraded in an eccentric vibromill with steel balls in steel drums. The amplitude of oscillations was 5 mm, and the frequency 50 c/s. The dispersion, unloading of the mill,

* Translated by R. J. Moseley from *Vysokomolekulyarnye Soedineniya*, Vol. 1, pages 865–868 (1959); RABRM translation No. 791.

TABLE I

PROPERTIES OF PRODUCTS OF MECHANICAL DEGRADATION

Original material	Duration of degradation, min	Properties of products of degradation: Molecular weight	Specific surface, m^2/g	Concentration of paramagnetic particles, g^{-1}
Polystyrene	0	180,000	—	None
	30	20,000	2–3	$4 \cdot 10^{18}$
Polyethylene	0	85,000	—	None
	40	—	—	$2 \cdot 10^{17}$
Barium sulfate	0	—	2	None
	20	—	17	$\sim 10^{17}$
Fused quartz	0	—	0.01	None
	20	—	7	$2 \cdot 10^{17}$

the first measurements of the EPR spectra and the determinations of the specific surface were all carried out in an atmosphere of argon at a temperature of −196°. The polymers investigated were organic polymers-emulsion polystyrene and low-pressure polyethylene—and an inorganic polymer—quartz (fused and crystalline). For the sake of comparison with crystals of ionic structure experiments were carried out with barium sulfate.

The properties of the materials before and after degradation are shown in Table I.

In every case we observe subsequently to degradation, accompanied by an increase in the specific surface and by a reduction in the molecular weight, the formation of electron paramagnetic resonance spectra (Figures 1 and 2).

Mechanical degradation of polystyrene at a low temperature leads to a reduction in the molecular weight approximately by a factor of 10, and to an increase in the specific surface up to 2 to 3 m^2/g. The width of the EPR spectrum line (Figure 1*a*) is 16–18 oersteds; the shape of the line is evidence of the anisotropy of the *g* factor. After unfreezing the specimens the intensity of the signal decreases sharply and after 5 to 7 min at room temperature the spectrum practically disappears.

The EPR spectrum of polyethylene at a low temperature (Figure 1*b*) is analogous to the spectrum of polystyrene. On heating to room temperature, when the intensity of the spectrum begins to decrease sharply, the signal changes into a symmetrical singlet with a line width of 22 oersteds (Figure 1*c*).

The occurrence of EPR spectra in organic polymers after mechanical deg-

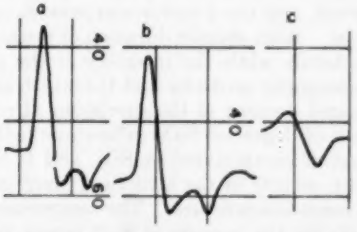

FIG. 1.—EPR spectra: *a*—polystyrene; *b*—polyethylene at −196°; *c*—the same at 30°.

radation may be explained by the formation of free macroradicals at the rupture points of the main carbon chain. The shape of the spectrum is possibly connected with the secondary reaction of the combination of oxygen occluded by the polymer, with a primary radical[9].

The shape, width and intensity of the line of comminuted barium sulfate at 77° K depend markedly upon the level of the high-frequency power. With high power (of the order of 10 mW) we observe saturation of the signal. With a sufficiently low level of power it is possible to avoid saturation and to obtain the true shape of an EPR line—a narrow singlet with a width between the points of maximum slope about 2 to 3 oersteds and with a g factor equal to the g factor of a free electron. On heating the specimen to room temperature the narrow signal disappears, and in its place we get an absorption band of width of some hundreds of oersteds. On repeated freezing the narrow signal appears once more. The narrowing of the spectrum at low temperature and the saturation of the signal are evidence that the main factor determining the width of the EPR line is the spin-lattice interaction; free electrons are apparently produced either by the fragmentation process or with electrostatic charges formed by friction.

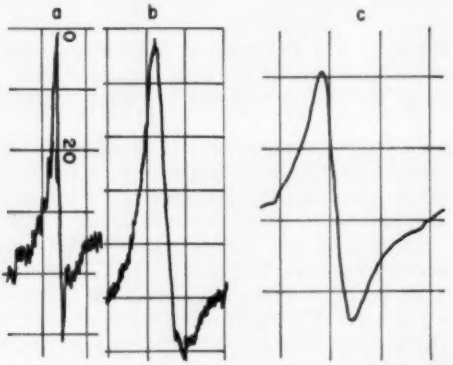

FIG. 2.—EPR spectra: a—$BaSO_4$ after degradation; b—original crystalline SiO_2; c—fused SiO_2 after degradation. All measurements at −196°.

In crystalline quartz (quartz sand from the Lyuberets workings) EPR spectra were observed before degradation (Figure 2b). After degradation in air the character of the spectrum changes fundamentally. The width of the EPR line of fused quartz after degradation (Figure 2c) is 8 ± 1 oersteds. Fine structure is not observed, and the g factor corresponds approximately to the g factor of a free electron. With shorter duration of degradation the parameters of the line remain as before while the intensity of the signal decreases. The concentration of paramagnetic particles and the width and shape of the signal do not alter on prolonged keeping of the specimens at room temperature.

The EPR spectrum of degraded SiO_2 differs markedly from the spectra of irradiated quartz[10] and of comminuted $BaSO_4$, and is hardly connected with electrons "trapped" by defects in the structure, since in this case wider lines would be observed at room temperature. The occurrence of the EPR spectrum is explained most easily by the rupture of Si-O bonds during degradation and by the existence of surface atoms with free valencies.

In the products of joint degradation of quartz with polymethyl methacrylate or polystyrene the content of macroradicals decreases several-fold, while the specific surface remains just as high.

These data indicate the possibility of recombination of vitrified radicals of different origin and suggest prospects for block-copolymerization of inorganic polymers (including so-called "fillers") with organic and elemental-organic polymeric substances.

CONCLUSION

By means of the method of electron paramagnetic resonance a demonstration is given of the occurrence of macroradicals during the degradation of glassy polymers whether of organic (polystyrene, polyethylene, polymethyl methacrylate) or of inorganic (quartz) nature.

ACKNOWLEDGMENT

In conclusion the authors express their thanks to L. A. Odintsov and E. L. Matveev for help in the experiments.

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MECHANOCHEMICAL PHENOMENA IN POLYMERS. II. THE EFFECTS OF INITIATORS AND INHIBITORS OF RADICAL PROCESSES *

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In the first article[1] of this series the influence of substances forming free radicals, or reacting with them, on the development of the mechanochemical processes during the milling of polymers was noted. This opens the possibility of regulating the properties of polymeric materials subjected to mechanical processing. In the present article are presented some results of a study of changes in the elastoviscous properties during the milling of rubbers with various inhibitors and initiators added, as well as changes in the dynamic fatigue life of vulcanizates as a function of the type of additive incorporated.

EXPERIMENTAL

Materials and methods of experimentation.—The main experimental material chosen was industrial styrene-butadiene rubber (SKS-30A). For comparison, tests were also made on natural rubber (NK). The additives chosen are inhibitors or initiators of the polymerization process. The additives and abbreviations to be used in this paper are: (1) benzoyl peroxide (BP), (2) dihydroxydiphenyl disulfide (DHPS), (3) bisazosiobutyronitrile acid, (4) di-*tert*-butylhydroquinone (DTBHQ), (5) tri-*tert*-butylphenol (BAIN), (6) polyethylene polyamine (PEPA), (7) (DP) Di-isopropylxanthogen disulfide (DIXD) (8) Santovar "O" (SO), (9) chlorinated paraffin (CP), (10) benzoquinone (BQ), (11) hydroquinone (HQ), (12) quinhydrone (QH), (13) acetoneanil (AA), (14) 2,2′-naphthyldisulfide (NDS). The additives were incorporated in the milling process on a cold mill.

The milling took place on a refiner rubber mill with 405 × 146 mm rolls with 1:1.22 friction ratio. Rubbers with the additives were milled on a cold rubber mill for an hour in air, with the stock at a temperature of 20–30° C. Then the progress of deformation with time was determined on a Goodrich plastometer[2] under the action of a pressure of 1 kg/cm and with subsequent load removal.

Besides this, vulcanizates were prepared from these same stocks by standard recipes, and were tested for fatigue life. For styrene-butadiene rubbers a recipe was used with 50 parts by weight of channel black and curatives consisting of MBTS, DPG and sulfur. The raw stocks were vulcanized by the usual method at 143° C for 80–100 minutes.

The fatigue resistance was determined by repeated stressing of samples in the form of dumbbell specimens with a deformation amplitude of 150% and a frequency of 250 cycles/min (at 20° C). The fatigue life (hours) of the samples to break was determined.

* Translated from *Zhur. Fiz. Khim.* **33** (3) 656–661 (1959).

An analogous work cycle was also carried out with natural rubber. Because of the difference between the chemical nature of styrene-butadiene and of natural rubber, somewhat different milling and vulcanizing conditions were used for them, as well as different compounding recipes. Thus, in contrast to SKS-30A, the period of incorporation of additives into natural rubber on the mill totaled 5 minutes. Such a short milling period for natural rubber is due to the rapid drop in the plasticity of its stock to values approximately comparable with those of the SKS-30A rubber. The natural rubber vulcanizates were prepared without carbon black, with sulfur and MBT as vulcanizing agents. The fatigue testing conditions for SKS-30A and NR vulcanizates were analogous.

The effect of additives in milling.—The change in properties as a result of the incorporation of active additives in milling is shown in Figures 1 and 2 for BP, DHPS and DNAB in quantities of 1 and 10 parts by weight on 100 parts of rubber.

An especially strong effect on SKS-30A is observed when BP is incorporated. It is interesting that when the quantity is changed, exactly opposite effects are obtained (Figure 1). It is characteristic that an increase in milling time markedly increases the effect of an additive on the properties (Figure 1). In the case of natural rubber the additive with the strongest effect is DNAB.

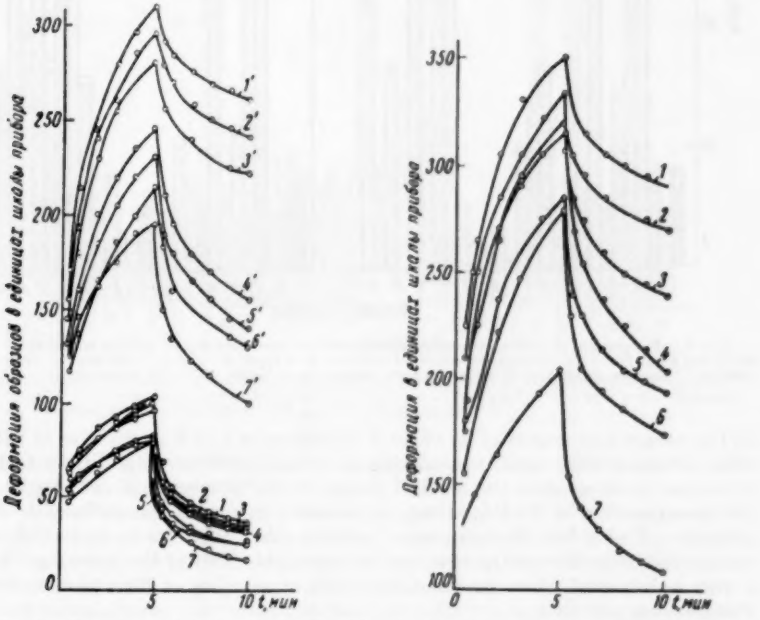

FIG. 1.—The progress of deformation of SKS-30A under the action of a constant pressure (1 kg/cm²) for a period of 5 minutes and after removing the load: *1*—1 part by weight of BP; *2*—with additive; *3*—10 parts by weight of DNAB; *4*—1 part of DNAB; *5*—1 part of DHPS; *6*—10 parts of DHPS; 7—10 parts by weight of BP (milling 5 min: 1′, 2′, 3′, 4′, 5′, 6′, 7′ the same after 60-minute milling). Abscissa: time, minutes; ordinate: deformation of samples in units of apparatus scale.

FIG. 2.—Progress of natural rubber deformation under the action of a constant pressure (1 kg/cm²) for a period of 5 minutes and after removing the load: *1*—1 part by weight of DNAB; *2*—without additive; *3*—1 part DHPS; *4*—1 Part of BP; *5*—10 parts of DHPS; *6*—10 parts of BP; 7—10 parts of DNAB. Abscissa and ordinate: as in Figure 1.

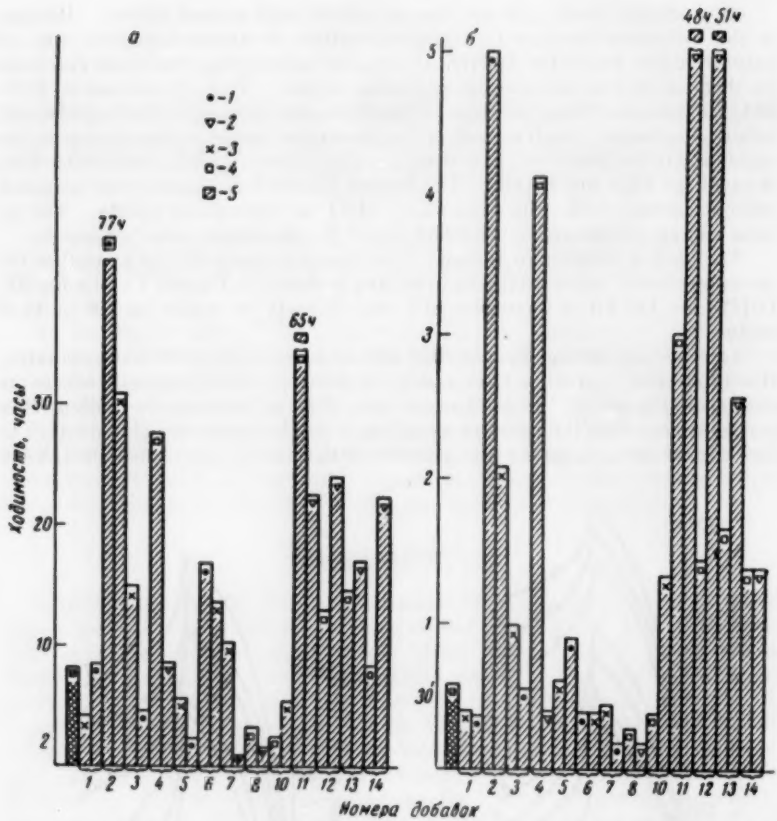

FIG. 3.—Fatigue life of vulcanizates of SKS-30A with the incorporation of various additives: *a*—at 20° C and *b*—at 100° C; *1*—10 parts by weight of additive; *2*—3 parts; *3*—1 part; *4*—0.3 part; *5*—without additive. Abscissa: number of additive; ordinate: fatigue life in hours. (77_4 = 77 hours, etc.).

In the nature and degree of its effect it is analogous to BP in the case of SKS-30A. Besides these additives, among the whole number of additives tested by us one must mention the marked change in the properties of raw stocks by the incorporation of PEPA, which appreciably increased the stiffness of the polymer. Di-*tert*-butylhydroquinone and the other quinones as a rule did not change the properties of the raw stocks appreciably, but at the same time had a very substantial effect on the fatigue life of samples of the corresponding vulcanizates.

The effect of additives in fatigue.—The process of fatigue is especially significant from the point of view of the effect of substances inhibiting and initiating free radicals upon the properties of polymers. In this case all the additives tested, without exception, change the fatigue life of the vulcanizates. Figure 3 shows data on the fatigue life of samples of SKS-30A vulcanizates with different additives (at 20° and 100° C). The additives DTBHQ, PEPA,

DHPS, HG, and AA substantially increase the fatigue life of samples of SKS-30A vulcanizates, while BP and TTBP reduce it.

Changes in fatigue resistance of vulcanizates of natural rubber with additives incorporated are given in Figure 4. Despite the rather large changes in the fatigue life of stocks from natural rubber upon the incorporation of DNAB and BP (in large quantities), the general situation in fatigue is more subdued than in the case of SKS-30A.

From the fatigue results one can see particularly distinctly the effect of concentration of the additives incorporated and of milling conditions in the preparation of the stocks. Thus for example, with the general tendency toward an increase in the fatigue life of rubber samples with DTBHQ, quantities of only 0.3–0.7 parts by weight give a marked increase in the fatigue life, to 1.5–2 times as much (Figure 5). It is interesting to note that even such small quantities

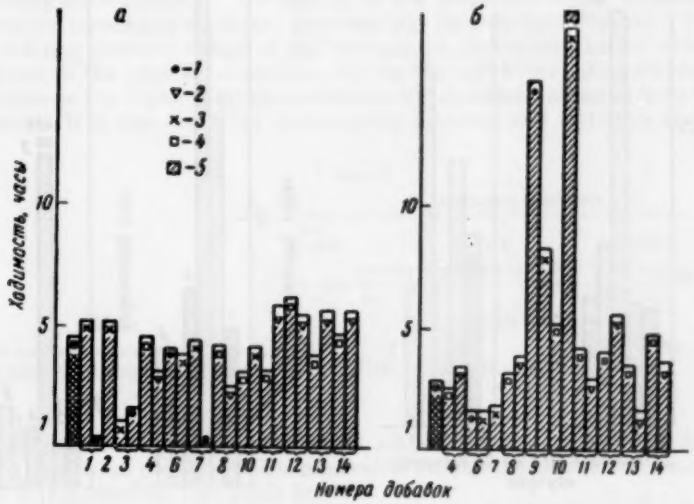

FIG. 4.—Fatigue resistance of NR vulcanizates with the incorporation of different additives: *a*—at 20° and *b*—at 100° C.; *1*—10 parts by weight of additive; *2*—3 parts; *3*—1 part; *4*—0.3 part and *5*—without additive. Abscissa: number of additive; ordinate: fatigue life, hours.

as 0.1 part by weight of DTBHQ on 100 parts of rubber have an influence on the fatigue life of samples at 100° C.

Analogous results on the increase in fatigue resistance of vulcanizates of SKS-30 A were obtained by adding small quantities of PEPA to the stock. The introduction of the PEPA was carried out both on cold (20–25° C) and on hot (80–90° C) mills. As Figure 6 shows, vulcanizates from hot and cold milling without additives (the cross-hatched bars) differ less from one another in properties than vulcanizates with the addition of PEPA. The most substantial increase in fatigue resistance was shown with quantities of PEPA not exceeding 1 part by weight on 100 parts of rubber, under cold milling conditions. Thus the data obtained indicate a substantial influence of initiating and inhibiting additives on raw rubbers and vulcanizates subjected to various kinds of mechanical action (milling of raw rubbers, fatigue of vulcanizates).

In connection with the results presented above, observations were made of the progress of mechanochemical processes in vulcanizates of the rubbers in their fatigue under especially severe dynamic conditions. For the fatigue testing the Martens-Schob[2] type of apparatus was used on the vulcanizates, in which massive specimens were subjected to the intensive action of large stresses caused by complex dynamic deformations of the vulcanizates, accompanied by the development of high temperatures (up to 200° C) in the center of the specimen. Depending on the intensity of the mechanical action, two types of break were observed in the specimens. Under the action of large stresses the specimens break even in the first few minutes of fatigue testing. The rupture has the nature of an explosion; the specimen flies into splinters with a previous forma-

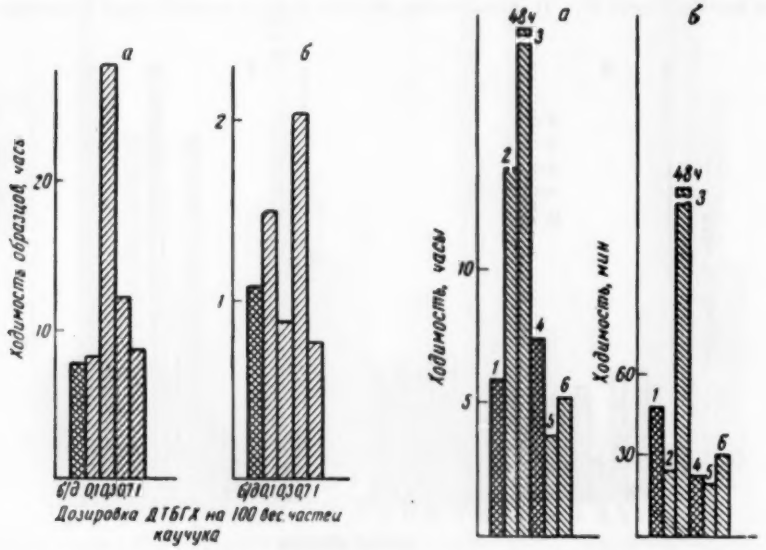

FIG. 5.—Fatigue resistance of SKS-30A vulcanizates with DTBHQ added: *a*—at 20° and *b*—at 100° C; 0 = without additive. Abscissa: Quantity of DTBHQ on 100 parts by weight of rubber; ordinate: fatigue life, hours.

FIG. 6.—Fatigue life of vulcanizates of SKS-30A with PEPA added: *a*—at 20° and *b*—at 100° C; *1*—without additive; *2*—0.3% PEPA; *3*—1% PEPA; *4*—without additive; *5*—0.3% PEPA; *6*—1% PEPA; 1, 2, 3.—cold milling; 4, 5, 6—hot milling. Ordinate: Left: fatigue life, hours; right: fatigue life, minutes.

tion of a cavity and with the evolution of smoke. Under the action of small stresses the specimens may operate for several days, and break by reason of an accumulation of structural changes which first cause a steady change in the shape of the specimen and an increasing stiffness of the rubber, then give rise to cracks and finally to rupture. Taking into account the high stress values, tests were made on stiff sodium polybutadiene and butadiene-methylstyrene synthetic rubber vulcanizates heavily loaded with inactive carbon blacks.

In this case it was observed (see Table) that the vulcanizate of butadiene-methylstyrene rubber, which in many of its properties is close to the vulcanizate of polybutadiene rubber, despite its higher heat buildup, has a considerably higher fatigue life under the same mechanical action, which does not cause in-

stant rupture. Thus the fatigue life of vulcanizates is not due directly to the quantity of their internal friction. In accordance with this, it is also found that the development of the explosive type of rupture in vulcanizates of butadiene-methylstyrene rubber vulcanizates requires the application of considerably larger forces than in the case of stocks of polybutadiene rubber. The introduction of initiator, for example, bisazoisobutyronitrile, into the vulcanizates catastrophically accelerates the rupture of the specimen in the case of the polybutadiene vulcanizate, but has a less substantial effect on the butadiene-methylstyrene rubber vulcanizate. At the same time, the incorporation of inhibitors, e.g., benzoquinone and DTBHQ, increases the fatigue life of samples of both types of rubbers (see Table I).

Thus the rupture of vulcanizates in fatigue testing is a typical mechanochemical process, which consists in the mechanical rupture of the chain molecules to form free radicals and a further development of chemical processes initiating these radicals. The change in the properties of the vulcanizates caused by these same secondary processes also leads to their rupture. Hence the differing chemical nature of the free radicals, determined by the chemical structure of the original rubbers (i.e., by the type of rubber) has a substantial influence on the degree of fatigue resistance of vulcanizates obtained from these rubbers. It is also clear that incorporating initiators and inhibitors of chain

TABLE I

	Designation of additive						
	No additive	DNAB			DTBHQ		BQ
	Quantity of additive in rubber, % by weight						
	—	0.1	1	2	5	0.3	0.5
	Fatigue life in minutes						
Polybutadiene rubber	1300	2	0.3	0.1	—	2500	2200
Butadiene-methylstyrene rubber	5400	5100	720	from 660 to 15	2	—	9200

radical processes into the stock should markedly change the course of the mechanochemical processes in the mechanical fatigue of vulcanizates, which we have in fact observed (see Table I).

Since the formation of free radicals by the scission of molecules is an irreversible process, it is connected to a certain degree with the internal friction of the vulcanizates, i.e., with the heat buildup. However, the fatigue of vulcanizates consists not only of the formation of free radicals, but also of the development of chain processes. The latter are not directly related to heat buildup, and hence no direct linear relation exists between heat buildup and fatigue, as was shown above. Besides this, the presence of inhibitors or initiators in the vulcanizate can, of course, markedly change the kinetics of the fatigue process, while having practically no effect on heat buildup.

CONCLUSIONS

1. The substantial effect of inhibitors and initiators of chain radical processes on the change in the properties of rubbers in milling, as well as on the resistance of vulcanizates to fatigue, has been shown. This indicates a mechanochemical mechanism of the processes occurring in processing polymers and of the fatigue of highly elastic materials (e.g., rubber vulcanizates). The act of

mechanical scission of chemical bonds, with the formation of free radicals which initiate the secondary chain processes, rests on these processes.

2. The possibility has been shown of regulating the properties of polymers in the course of their industrial processing, and also of increasing the dynamic fatigue resistance of vulcanizates by incorporating small quantities of additives active in regard to free radicals.

ACKNOWLEDGEMENT

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MECHANOCHEMICAL PHENOMENA IN POLYMERS. III. STRENGTH OF THE BOND BETWEEN ELEMENTS OF MULTIPLY POLYMER ARTICLES *

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A very interesting question which so far has had little attention is that of the strength of the bond between individual elements of multiply articles, such as tires. A fundamental difficulty in its solution is that the bond strength between the various layers of such articles depends essentially upon many factors. As a result of a series of papers[1] data are available on the noteworthy influence upon the strength of the bond between the rubbers exerted by alterations in the formula, in the parameters of the manufacturing processes, in the physicochemical characteristics, and also in the construction of the articles and in other factors.

The cause of the service failure of multiply vulcanized rubber articles is in the majority of cases not the natural wear of the rubber, but the separation of the elements or stripping of the rubber from the cord. This phenomenon takes place not at once, but only after a considerable number of deformations. Consequently ply separation occurs as the result of the development of the process of fatigue of the material at the boundary of two rubbers, i.e., in the joint zone. With repeated deformations of the article there develops a process of alteration, i.e., fatigue of the polymer, leading ultimately to the failure of the joint.

As is well-known[2–4], under conditions of repeated deformations under the action of mechanical forces the chain molecules of the polymer are broken with the formation of free radicals at the ends of the broken chain. The appearance of free radicals leads to the development of secondary chemical processes, leading to failure of the article. Thus to enhance bond strength between vulcanized rubber elements it is necessary, as in other cases of the development of fatigue[4] to prevent the occurrence of free radicals, i.e., to add to the vulcanized rubber inhibitors reacting with chain end radicals[5].

It was therefore of interest to attempt to find such inhibiting substances, which, by preventing the development of the secondary chain chemical processes initiated by the mechanical scissions of the molecules, would exert a favorable influence upon the bond strength between different vulcanized rubbers. In this way it appears possible to enhance considerably the serviceability of multiply vulcanized rubber articles, in particular tires, and also to explain the nature of the principal processes developing in the joint zone of two different polymeric materials and responsible for its separation.

EXPERIMENTAL

Objects and method of investigation.—The investigation of the action of the inhibitors of radical processes upon bond strength was carried out on specimens

* Translated by R. J. Moseley from *Zhur. Fiz. Khim.* 33, 793–8 (1959); RABRM Translation 782.

of filled stocks (tread type) based on ordinary styrene-butadiene rubber (SKS-30A) and an oil-extended SKS-30AM. In the majority of cases a bonding agent is used in the building of multiply rubber articles for the plyingup of the different plies of rubber. For this reason we prepared test specimens with a layer of ordinary bonding agent and of a bonding agent containing an inhibitor. The bonding agents were prepared from filled stocks based on natural rubber and on SKS-30A. The bonding composition was first given 2 or 3 passes on the mill to produce a thin sheet, after which it was dissolved in naphtha in the normal proportion. After complete dissolution of the bonding agent a definite amount of inhibitor was added to the solution.

It is a well-known fact that quinones, polyolefins and aromatic amines are good inhibitors of chain processes[6–8]. Thus, as our inhibitors we selected a mixture of polyethylene polyamines, 2,5-di-*tert*-butylhydroquinone, dinaphthyl disulfide, tri-*tert*-butylphenol, benzoquinone, acetonanil, and hydroquinone, which we added to the bonding agent in various amounts.

The specimens were prepared in the form of sheets of vulcanized rubber, 175 × 90 × 36 mm, composed of two identical layers, between which the layer

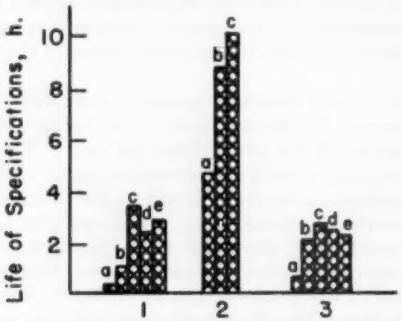

FIG. 1.—Alteration in bond strength of pliedup specimens based on SKS-30A on the addition of various additives to the bonding layer: *1*—specimens with bonding layer based on natural rubber with polyethylene polyamine; *2*—specimens with bonding layer based on SKS-30A with di-*tert*-butylhydroquinone; *3*—specimens with bonding layer based on natural rubber with di-*tert*-butylhydroquinone. The amount of additive in parts by weight to 100 parts by weight of rubber in the bonding agent: *a*—without additive; *b*—1; *c*—3; *d*—5; *e*—10.

of bonding agent was applied at the time of building. The plates were vulcanized at 143° C and a pressure of 20 atmospheres for 100 min. From them were cut specimens which were tested for dynamic ply separation on a De Mattia machine with maximum compression of up to 40% of the height of the specimen and frequency 500 c/min.

The test specimens were cubes of 25 mm edge, the bonding agent layer following the diagonal section of the cube. With this arrangement of the layers there takes place on the boundary the maximum possible shear deformations, which fact considerably reduces the duration of testing.

The addition to a bonding agent based on natural rubber of tri-*tert*-butylphenol, dinaphthyl disulfide, benzoquinone, acetonanil or hydroquinone did not under the fatigue conditions in question exert a significant influence upon the bond strength of pliedup specimens whether based on SKS-30A or SKS-30AM. A considerable increase in bond strength of pliedup specimens was found on adding polyethylene polyamine to a natural rubber-based bonding agent, in

comparison with the bond strength of the same specimens with a bonding agent based on natural rubber without any addition.

The bond strength of the specimens alters depending on the amount of polyethylene polyamines added to the bonding layer. We tested pliedup specimens with a bonding layer containing 1, 3, 5 and 10 parts by weight of polyethylene polyamine to 100 parts by weight of rubber in the bonding agent.

The results show that the optimum amount, increasing the bond strength approximately 10-fold, for specimens based on SKS-30A, and also on SKS-30AM (Figure 1), is 3 parts by weight of polyethylene polyamine to 100 parts by weight of rubber added to the bonding agent.

We investigated the influence of di-*tert*-butylhydroquinone upon the bond strength of pliedup specimens based on SKS-30A when added to bonding agents based on natural rubber and on SKS-30A (Figure 1). The di-*tert*-butylhydroquinone was added to the natural rubber bonding agent in 1, 3, 5 and 10 parts by weight of rubber.

As we may see from Figure 1, di-*tert*-butylhydroquinone also increases the bond strength of pliedup specimens, the optimum amount being 3 parts by weight to 100 parts by weight of rubber. With this amount the bond strength is increased approximately 5 to 6-fold.

It must be noted that the same amounts of di-*tert*-butylhydroquinone in a bonding agent of natural rubber were used for the investigation of their influence upon the bond strength of pliedup specimens of SKS-30AM rubber.

The bond strength in this case increases by 2 to 3 times, the optimum amount being the same as for SKS-30A.

An investigation of the influence of di-*tert*-butylhydroquinone upon the bond strength of pliedup rubbers based on SKS-30A with a bonding layer of SKS-30A was carried out for two different contents: 3 and 10 parts by weight to 100 parts by weight of rubber in the bonding agent. As may be seen from Figure 1, the bond strength in the present case again increases noticeably. We must remark here that a bonding agent based on SKS-30A does not lower the bond strength in dynamic ply separation of pliedup specimens so noticeably as a bonding agent based on natural rubber. We may indirectly judge the increase in the bond strength of pliedup specimens containing di-*tert*-butylhydroquinone in a bonding layer based on SKS-30A from the fact that the majority of the specimens with this additive fail not in the joint but in the

TABLE I

DURATION OF TESTING UP TO FAILURE, AND NATURE OF FAILURE OF PLIED-UP SPECIMENS

Pliedup specimens	Duration of testing of specimens failing at the joint, h	Failure in the rubber, %
Without bonding layer	9.4	100
With bonding layer without additions	4.5	69
With bonding layer with 3 parts by weight of di-*tert*-butylhydroquinone	8.5	58
With bonding layer with 10 parts by weight of di-*tert*-butylhydroquinone	10	95.5

rubber itself, whereas specimens prepared with a bonding agent not containing the additive frequently fail in the joint (see Table I).

The addition of di-*tert*-butylhydroquinone by 10 parts by weight to 100 parts by weight of the rubber in the bonding agent brings the bond strength of pliedup specimens close to that of solid specimens.

The influence of di-*tert*-butylhydroquinone upon bond strength between vulcanized rubbers was investigated also in the case of its addition to a bonding mixture based on natural rubber, directly during the mixing. In this case the influence of the addition upon the bond strength is once again favorable, i.e., the working life of the specimen up to failure increases approximately three-fold.

It must be noted that when adding the inhibiting additive to the bonding agent during mixing a portion of it may be used up in the actual process of mixing[9, 10], since this process also involves the formation of free radicals. Therefore the optimum amounts of additive may differ according to whether added in the mixing process or in the process of dissolving the bonding mixture. In fact, to get an improvement in the results it was found necessary to add some-

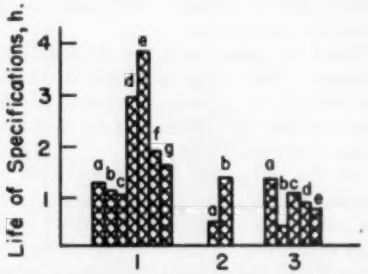

FIG. 2.—Alteration in bond strength of pliedup specimens based on SKS-30A on the addition of di-*tert*-butylhydroquinone: *1*—specimens with bonding layer based on natural rubber with additive added to the bonding agent during mixing. The amount of additive in parts by weight to 100 parts by weight of rubber in the bonding agent: *a*—without additive; *b*—1, *c*—3, *d*—4, *e*—5, *f*—6, *g*—10. *2*—Specimens with bonding layer based on natural rubber (without additive) with addition of 0.3 parts by weight of additive to 100 parts by weight of the rubber in the stock for the body of the article: *a*—without additive; *b*—with additive. *3*—Influence of duration of milling upon specimens with bonding layer based on natural rubber (without additive) containing 3 parts by weight of additive to 100 parts by weight of rubber in the stock for the body of the article: *a*—without additive; *b*—with additive; *c, d, e*—with additive and additional milling for 10 min., 1 h, and 3 h respectively.

what large amounts of additive to the bonding mixture during mixing. We settled on an amount of 5 parts by weight of additive to 100 parts by weight of the rubber in the bonding agent for SKS-30A vulcanizates and 10 parts by weight for SKS-30AM. The results of these tests are given in Figure 2.

On adding di-*tert*-butylhydroquinone directly to the stock for the specimens the bond strength increases even when a bonding agent without additive is employed. However in this case there is an optimum dose. Thus, for instance, with a dose of 0.3 parts by weight of di-*tert*-butylhydroquionone to 100 parts by weight of rubber in the stock the bond strength of pliedup specimens increases approximately three-fold (Figure 2). On adding 3 parts by weight of di-*tert*-butylhydroquinone to 100 parts by weight of the rubber in the stock the bond strength falls off noticeably.

All this confirms the idea that in the milling of a stock there are formed free radicals reacting with inhibitors. Since milling may cause consumption of inhibitor and consequently reduce the amount of inhibitor in the stock, the

bond strength of pliedup rubber specimens may alter with further milling. As a result of this the influence of the inhibitor upon the bond strength must first increase and then with further milling decrease. Such an effect of milling upon bond strength is demonstrated in Figure 2.

ASSESSMENT OF RESULTS

From the data we have amassed there appears a noticeable influence of certain substances which inhibit chain radical processes upon the bond strength of vulcanized rubbers of different nature in repeated deformations. It follows that the rate of the process of destruction of the joint of two elastic polymers does in fact depend essentially upon the development of chain radical processes. Since the formation of free radicals in the joint zone is governed by mechanical influences (repeated deformations), the main mechanism of the phenomenon is quite evident; the mechanical influences, causing the scission of chain molecules with the formation of free radicals, are concentrated in the region of the joint, which happens to be the region of non-uniformity of mechanical properties of a deformed multiply article. As a result of this there are formed in the joint region a large number of free radicals. Therefore the secondary chain processes initiated by these radicals cause the greatest alteration in properties in the joint zone, which leads in turn to a more rapid process of development of fatigue, and then of failure in this zone. Therefore the mechanism of failure along the edges of a multiply elastomeric article, i.e., socalled "separation at the joint", resolves itself into the mechanism of fatigue of polymers, already described[2–4], characterized by nonuniformity of distribution of the mechanical stresses, governed by the difference of elastic properties combined in one article of various materials.

The ideas developed above of the mechanism of ply separation of multiply elastic polymeric articles under repeated deformations open up the possibility of a rational approach to the solution of increasing the service life of such articles. Since the primary act leading to ply separation is the mechanochemical act of mechanical scission of chemical bonds in the chain or crosslinking structures of the polymers, it is evident that two ways of increasing the service life of the articles are possible—either a reduction in the number of acts of scission as a result of reduction in the intensity of mechanical action, or else the suppression of secondary chemical chain processes initiated by the free radicals formed in the scission of the chemical bonds. The former calls for designs of multiply vulcanized rubber articles subject in service to minimal mechanical action. Moderation of the technical influences is possible also by appropriate alteration in the general design of the mechanisms in which the multiply elastic parts are employed.

The latter way is of purely chemical nature; it is based on the inhibition of free radicals. As may be seen from our data, it is possible by the addition of inhibiting substances to enhance considerably the service life of elastic articles under repeated deformations. However it becomes necessary to determine the optimum amount of inhibitors, which depends, naturally, upon the number of free radicals formed per unit of time in a unit of volume of the polymer, i.e., it depends upon the pattern of mechanical action. The question of the selection of effective inhibitors is also very important, since free radicals of differing chemical structure may occur depending upon the chemical structure of the polymer. Consequently, different polymers have differente ffective inhibitors. In addition, in selecting inhibitors it is necessary to take into account the tem-

peratures at which they are to take effect, i.e., to take into account the working temperature of a multiply article, which depends upon the character of the deformation (as a result of liberation of heat during the deformations), upon the dimensions and shape of the article (as a result of the poor thermal conductivity of polymers) and also upon external conditions (the temperature of the surrounding medium, the conditions of heat exchange of the article with the medium, etc.).

The investigation of these processes, which is of great importance in enhancing bond strength between the plies of a multiply elastic article, is at the same time of considerable interest in extending our conceptions of the chemical properties of free radicals.

CONCLUSIONS

1. The basis of the process of ply separation of multiply rubber articles under repeated deformations is fatigue of the material in the region of the joint of the plies, which is a mechanochemical process, as previously studied[2–4], consisting of the development of chain chemical processes initiated by free radicals which are formed in the mechanical scission of chemical bonds in the molecules.

2. By the addition of substances inhibiting chain radical processes to the polymer it is possible to raise considerably the strength of the bond between elements of multiply vulcanized rubber articles.

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MECHANOCHEMICAL PHENOMENA IN POLYMERS. IV. MODIFICATION OF RAW AND VULCANIZED RUBBERS *

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It has been demonstrated[1–6] that free radicals are formed as a result of mechanical action in raw and vulcanized rubbers. Consequently it becomes possible to initiate polymerization by mechanical action[7].

It was thought essential to assess the development of mechanochemical processes in vulcanized and raw rubbers in the presence of low-molecular substances which are capable of polymerizing.

EXPERIMENTAL

Method.—Mechanical destruction of the materials was carried out on laboratory micro-mills and also in a high shear plasticator called a "modifier", constructed in the Institut Plastmass[8]. It could be operated in a nitrogen atmosphere.

The main working part of the device—the scroll—consists of two parallel discs placed one over the other. On the discs there is cut a thread of different cross section in the form of a spiral.

The lower disc rotates at a rate of 30 rpm, while the upper is stationary. The apparatus is rendered pressure tight to make it possible to operate in a current of nitrogen and other gases. The upper and lower discs have jackets for cooling or heating.

In our experiments we used cooling with a strong current of running water, which made it possible to work at a constant temperature of 18 to 20° C.

The weight of the specimens put into the device was 10 to 20 g.

The rolls of the micro-mill were 180 × 80 mm with friction ratio 1:1.11. The gap was less than 1 mm.

The duration of mechanical action of the "modifier" and rolls was varied from 5 to 30 min and more.

The main objects of investigation were commercial raw rubbers and standard vulcanized rubbers based on SKS-30A (styrene-butadiene rubber) and SKB (sodium butadiene rubber). The vulcanizates were prepared from standard recipes.

Assessment of properties was carried out mainly from the mechanical characteristics of vulcanizates prepared from these products after the mechanical treatment in question, and also from their life under repeated extension of specimens by 100% to 250 c/min. In individual cases we assessed the solubility and determined the viscosity of the solutions, and also the swelling in organic solvents.

* Translated by R. J. Moseley from *Zhur. Fiz. Khim.* **33**, No. 5, 988–91 (1959); RABRM Translation 783.

TABLE I

MODIFICATION OF VULCANIZED RUBBERS BY MONOMERS

Starting materials	Processing conditions (15 min at 18–20° C)	Duration of vulcanization min. 143° C	Mechanical properties of vulcanizates of mechanochemical copolymers							
			Modulus kg/sq cm for extension				Tensile strength, kg/sq cm	Relative elongation %	Permanent set, %	Fatigue life, min
			100%	200%	300%	400%				
SKB	Modifier, nitrogen	15	40	—	—	—	111	196	13	3
77% SKB +23% styrene	Modifier, nitrogen	15	36	110	—	—	143	244	10	6
77% SKB +23% methyl methacrylate	Modifier, nitrogen	15	34	89	—	—	138	260	11	2
SKB	Rolls, air	15	50	—	—	—	66	140	4	0
77% SKB +23% styrene	Rolls, air	15	22	61	116	—	155	340	20	38
77% SKB +23% vaseline oil	Rolls, air	15	11	37	—	—	71	288	10	100
SKS-30A	Modifier, nitrogen	25	44	91	—	—	140	322	8	2
Standard SKB	Without processing	45	18	42	75	113	147	508	21	25

The experiments were carried out as follows: the specimens of raw or vulcanized rubber, cut up finely, with the addition of monomers (styrene and methyl methacrylate) or other substances were treated in the modifier or on the rolls in an atmosphere of nitrogen or air. The properties of the final vulcanizates based on the resulting mechanochemical copolymers were determined by the ordinary methods used in standard tests of vulcanized rubbers (we assessed the values of the modulus and the tensile characteristics).

MODIFICATION OF VULCANIZED RUBBERS BY THE MONOMERS

In Table I we present the results of the mechanochemical reaction of the specimens of standard vulcanizates of SKB with styrene and methyl methacrylate. The amount of the monomer corresponded to 30 parts by weight to 100 parts by weight of the original vulcanized rubber, i.e., it was 23% by weight.

Vulcanized rubbers previously swollen in monomer was processed in the "modifier" or on the mill for 15 min in a current of nitrogen or in air. From the processed vulcanized rubbers we prepared in air stocks and vulcanizates following the formula ordinarily used for reclaim (without carbon black).

The data presented show that as a result of mechanochemical reactions proceeding both in nitrogen and in air there occurs a marked raising of the strength of freshly vulcanized rubbers by 30 to 60 kg/sq cm and an increase in the relative elongation at break. At the same time there is a considerable improvement in the life of the specimens under repeated deformation. For the sake of comparison we present data for a standard vulcanizate of SKB and reclaim (SKS-30A).

The characteristics of mechanochemical polymers produced by reaction of vulcanizates of SKB with monomers agree well enough with the data for SKS-30A and approximate tensile and fatigue properties of standard SKB vulcanizates.

Thus mechanochemical copolymerization of vulcanized rubbers with monomers makes it possible to produce reclaim rubbers with improved mechanical properties.

MODIFICATION OF RAW RUBBERS BY MONOMERS

A series of experiments was carried out on the production of mechanochemical copolymers of raw rubbers with styrene and methyl methacrylate. The results are presented in Table II.

For these experiments we took sodium butadiene rubber, not prepared with PBNA. The amount of monomers was 9, 17 and 23% by weight. The duration of mechanical processing of the swollen specimens of raw rubber in the nitrogen modifier was 15 min. From the processed swollen rubbers we prepared vulcanizates according to the standard recipe.

It may be seen from the data presented that the tensile strength of the vulcanizates of the mechanochemical copolymers is enhanced. Naturally the moduli also increase, and the fatigue strength under repeated extension increases.

The addition of these same monomers to the raw rubber on the mill in the presence of air gives vulcanizates with inferior mechanical properties.

The styrene-butadiene rubbers were processed only with methyl methacrylate.

TABLE II

MODIFICATION OF RAW RUBBERS BY MONOMERS

Starting materials	Processing conditions (at 18–20° C)	Duration of vulcanization min, 143° C	Mechanical properties of vulcanizates of mechanochemical copolymers							
			Modulus kg/sq cm for extension				Tensile strength, kg/sq cm	Relative elongation %	Permanent set, %	Fatigue life, min
			100%	200%	300%	400%				
SKB	15 min, modifier, nitrogen	50	27	62	99	145	149	428	26	29 min
91% SKB + 9% styrene	Modifier nitrogen	50	21	42	71	105	154	564	48	42 h
77% SKB + 23% styrene	Modifier, nitrogen	50	49	99	149	—	178	380	24	—
91% SKB + 9% methyl methacrylate	Modifier, nitrogen	50	31	65	112	—	163	420	36	1 35 min
83% SKB + 17% methyl methacrylate	Modifier, nitrogen	50	31	61	104	149	177	484	44	2 hr 54 min
77% SKB + 23% methyl methacrylate	Modifier, nitrogen	50	47	103	169	—	172	324	22	80 min
77% SKB + 23% vaseline oil	Modifier, nitrogen	50	2	12	23	42	62	556	27	10 min
91% SKB + 9% styrene	30 min, rolls, air	50	22	47	80	116	132	460	38	4 h 20 min
83% SKB + 17% styrene	Rolls, air	50	29	59	101	143	166	452	36	7 h 24 min
83% SKB + 17% methyl methacrylate	Rolls, air	50	25	52	93	140	149	436	30	1 h 43 min
91% SKS-30A + 9% methyl methacrylate	Rolls, air	80	15	23	39	69	290	820	51	—
SKS-30A	Without processing	80	12	27	54	85	254	764	39	1 h 37 min

ASSESSMENT OF RESULTS

The data obtained clearly indicate the possibility of a considerable alteration in the properties of raw rubbers and of the products of mechanical processing of vulcanizates by utilizing mechanochemical reactions in such materials, impregnated with substances which are capable of polymerizing.

In particular the data in Table I are evidence that as a result of heavy mechanical processing of vulcanized SKB rubber in the presence of styrene in the modifier or on the mill a polymer is formed which is analogous to a mechanically processed vulcanizate of styrene-butadiene rubber. This indicates that interaction of the butadiene rubber with styrene has taken place during the mechanical processing.

It is interesting to note that processing an SKB vulcanizate impregnated with vaseline oil (paraffin oil RJM) gives a totally dissimilar product, since the vaseline oil is not capable of polymerizing, and consequently does not favor the development of chain processes initiated by mechanical scissions of polymer molecules. On the other hand, after processing this oil has an obvious plasticizing effect which is absent with processed rubbers impregnated with polymerizing substances (styrene or methyl methacrylate). (The plasticizing effect in the swelling of vulcanized rubbers in styrene or methyl methacrylate is observed only in the first stage of the process before the mechanical processing.)

The data in Table II clearly indicate the extensive possibilities of altering the properties of raw rubbers by processing them together with monomers.

Thus the technical processes of processing polymers, which were at one time regarded as leading to deterioration in structural characteristics (increasing branching, oxidation and so on), may be utilized also to improve the structure of the polymer molecules. This improvement, based on mechanical initiation of chain radical processes which lead to the synthesis of a new polymeric substance during processing of polymers swollen in various monomers, manifests itself naturally in a considerable alteration in the physical and mechanical properties of the processed polymer.

These results indicate the possibility of deliberate alteration in the properties of processed polymers directly during the processing, and also of improving reclaim, produced by mechanical methods, of rubber and other polymers.

CONCLUSIONS

1. Mechanical processing of polymers swollen in substances capable of polymerizing leads to the development of processes of radical polymerization initiated by mechanical scission of chain molecules. The new polymeric substances thus formed have a correspondingly altered set of properties.

2. Processes of manufacturing polymers which are closely connected with the development of mechanochemical processes may be used to improve the properties of the processed polymer.

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PRODUCTION AND PROPERTIES OF BLOCK POLYMERS

B. M. Kovarskaya, L. M. Golubenkova, M. S. Akutin and I. I. Levantovskaya

Of all the known methods for the production of block and graft polymers (chemical, mechanochemical, radiation, and so on) the greatest importance from the point of view of simplicity of carrying out a commercial process attaches to the mechanochemical method. In the present investigation this method of producing block polymers was empolyed with special apparatus, making possible a more intensive distribution of the material in a medium of inert gas in a laboratory "modifier", described previously[1, 2], and in a continuous "modifier", consisting of a combination of a screw and a scroll and making it possible to work either at room temperature or with heating up to 200°. The continuous modifier was designed in the Nauchno-Issled. Inst. Plastiche-skikh Mass under the supervision of M. P. Shapenkov.

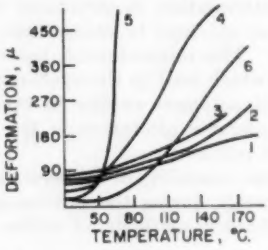

Fig. 1.—Dependence of deformation upon temperature for a block polymer, *6*, based on novolac Resin-17 and SKN-26, ratio 1:1, and for its fractions, *1*, *2*, *3*, *4* and *5*.

Using the apparatus indicated, it is possible in practice to combine various polymers with each other: low-molecular weight resins with elastic high-molecular weight products, high-molecular weight substances of different chemical nature, polymers with monomers and so on.

The present purpose was the investigation of block polymers whether produced on the laboratory modifier or on the continuous modifier. The polymers of the investigation were: a block polymer based on the phenol-xylol formaldehyde "Resin-17" and SKN-26 butadiene-nitrile rubber, produced on the laboratory modifier in 15 min with water cooling with various proportions of the original components, and a block polymer based on block polystyrene and SKN-26 butadiene-nitrile rubber, produced on the continuous modifier at a temperature of 140° and passage of the material through the modifier in 5 to 7 min.

* Translated by R. J. Moseley from *Vysokomolekularnye Soedineniya* 1, 1042–7 (1959); RABRM translation 788.

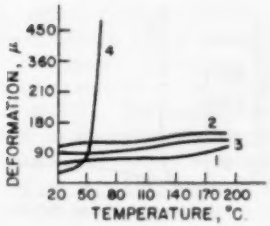

FIG. 2.—Dependence of deformation upon temperature for fractions, *1*, *2*, *3*, *4*, of a mechanical mixture of Resin-17 and SKN-26, ratio 1:1.

The block polymers were investigated by the thermomechanical method, by the method of turbidimetric titration and by means of infrared spectroscopy.

The investigation of the block polymers produced by the mechanochemical method presents considerable difficulties in view of the complexity of separating them from the mechanical mixture of homopolymers.

The phenol-rubber block polymer produced in the modifier was separated from the mixture of homopolymers by fractionation from an acetone solution by water.

The thermomechanical curves of the specimens were plotted on a dynamometric balance[3] at a stress $\sigma = 0.07$ kg/sq cm.

In Figures 1 and 2 we present the thermomechanical curves of fractions of a block polymer and of a mechanical mixture of SKN-26 and Resin-17 for ratio of original components 1:1. The mixture was prepared by bonding acetone solutions of homopolymers in appropriate proportions. The raw rubber was processed in the modifier before dissolution.

As may be seen from Figure 2, the mixture separates in practice into fractions characteristic in their thermomechanical behavior of a novolac resin (Figure 2, curve *4*) and of raw rubber (Figure 2, curves *1*, *2* and *3*). In fractionation of a block polymer and the remaining unreacted homopolymers we get, together with fractions characteristic of the raw rubber (Figure 1, curve *1*) and the resin (Figure 1, curve *5*), fractions which combine the properties of the original substances (Figure 1, curves *2*, *3* and *4*); these fractions are capable

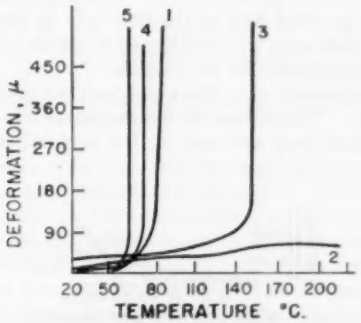

FIG. 3.—Dependence of deformation upon temperature for a block polymer, 1, based on Resin-17 and SKN-26, ratio 5:1, and for its fractions, *2*, *3*, *4*, *5*.

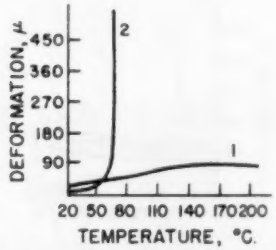

FIG. 4.—Dependence of deformation upon temperature for fractions, *1*, *2*, of a mechanical mixture of Resin-17 and SKN-26, ratio 5:1.

of flow at low stresses and comparatively low temperatures, whereas under these conditions raw rubber does not pass into the viscous-flow state.

An analogous thermomechanical picture is observed for fractions of block polymer and mixture with a 5:1 ratio of Resin-17 and SKN-26 (Figures 3 and 4).

In the present case a mechanical mixture also separates completely into two fractions on fractionation—resin (Figure 4, curve *2*) and rubber (Figure 4, curve *1*). The block polymer (Figure 3, curve *1*) contains fractions, characteristic of rubber (Figure 3, curve *2*) and of resin (Figure 3, curve *5*) and fractions combining the properties of the original substances (Figure 3, curves *3* and *4*).

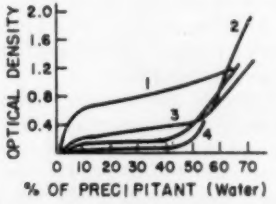

FIG. 5.—Curves of the turbidimetric titration: SKN-26, *1*, novolac Resin-17, *2*, block polymers based on Resin-17 and SKN-26, with ratios 1:1, *3*, 5:1, *4*.

From Figures 1 to 4 it is evident that the thermomechanical behavior of the fractions of the block polymer and of the fractions of the mechanical mixture differs sharply, which indicates the occurrence of a new type of polymer during the processing of homopolymers in the modifier.

To confirm the occurrence of a block polymer we used also the method of turbidimetric titration. The curves of the turbidimetric titration were determined both for the block polymer and for the original components and for a mixture of them.

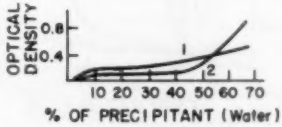

FIG. 6.—Curves of turbidimetric titration of a block polymer based upon novolac Resin-17 and SKN-26, with ratio 5:1, *1*, and of a mechanical mixture of the same substances, *2*.

The titration was carried out with a SF-4 spectrophotometer in a specially designed glass vessel provided with a jacket for thermostatic control of the solution. The use of the SF-4 spectrophotometer and the special vessel for turbidimetric titration was proposed by A. N. Shabadash. The tests were carried out at a temperature of 30°. The turbidimetric titration was effected from 0.01% acetone solutions, using water as precipitant.

In Figures 5 and 6 we present the turbidimetric curves of block polymers, mixtures and original homopolymers. On the abscissae we plot the percentage of the precipitant, and on the ordinates the optical density of the solution[4, 5].

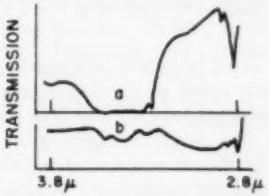

FIG. 7.—Infrared spectra: *a*—SKN-26, *b*—novolac Resin-17.

The turbidimetric curves for block polymers not freed from the mixture of homopolymers have two points of inflection characteristic of rubber and of novolac resin (curves *3* and *4* of Figure 5), and have no point of inflection characteristic of the third component, since the block polymer obtained and the original rubber are apparently similar in solubility and molecular weight. These curves have common character but differ somewhat as a function of the ratio of the original components.

In Figure 6 we present the curves for turbidimetric titration of a mechanical mixture of Resin-17 and SKN-26 (ratio 5:1) and of a block polymer for the

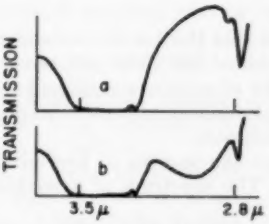

FIG. 8.—Infrared spectra; *a*—precipitated mechanical mixture; *b*—block polymer based upon Resin-17 and SKN-26.

same ratio of components. In this case the block polymer could be separated only from one of the original substances, the resin. It was not found possible to separate the block polymer from the rubber on account of the similarity of solubility. Therefore the turbidimetric curve of the block polymer (curve *1* of Figure 6) has no point of inflection characteristic of the resin, and differs in this way from the curve for a mechanical mixture of the original substances.

Investigation of the solubility of the products obtained after processing in the laboratory modifier showed that for any given ratio of the original components 15 to 20% of the resin combines with the rubber.

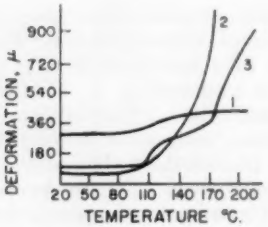

FIG. 9.—Dependence of deformation upon temperature for SKN-26, *1*, block polystyrene, *2*, and a block polymer based on these substances, *3*, at a 1:1 ratio.

For the phenol-rubber block polymer produced on the laboratory modifier and the mechanical mixture (with ratio of the original components 1:1) we plotted the spectra in the infrared range. For this the specimens were prepared in the form of thick films (0.5 mm) for observation of the bonded hydrogen hydroxyl even with an insignificant amount of novolac resin in the specimens. Prior to this we had obtained the spectra of the original components in the 3μ range employing a LiF prism (Figure 7).

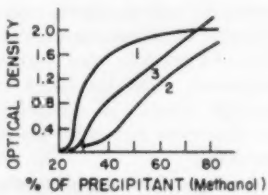

FIG. 10.—Curves of the turbidimetric titration of block polystyrene, *1*, SKN-26, *2*, and *3*, a block polymer based on these substances, ratio 1:1.

In order to demonstrate that the novolac resin is in fact a component part of the block polymer, we selected the hydrogen bonded hydroxyl band (2.8 to 3.1μ), which is characteristic of a novolac resin and absent in the case of rubber. The block polymers and mechanical mixture were repeatedly precipitated with methanol from acetone solutions.

In Figure 8 we present the spectra of precipitated specimens of a block polymer and a mixture. The spectrum of a mixture of rubber and novolac

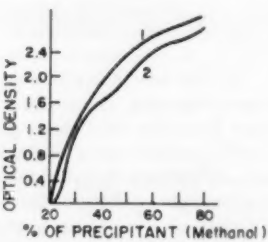

FIG. 11.—Curves of the turbidimetric titration of a block polymer, *1*, and mechanical mixture, *2* based upon block polystyrene and SKN-26, ratio 1:1.

resin, even after two-fold precipitation, does not display the hydroxyl band (Figures 10 and 11) are presented for a block polymer based on block poly- (Figure 8, *a*). The presence of the hydroxyl band in the specimen of the repeatedly precipitated product may be taken as an indication that a block polymer has been produced.

Thus, these investigations show that in the mixing of phenol-xylolformaldehyde resin and butadiene-nitrile rubber in a laboratory modifier there takes place the formation of a block polymer.

In the continuous modifier we produced various block polymers—on the basis of polystyrene and butadiene-nitrile rubber, of polystyrene and PVC, of phenol-formaldehyde epoxide resins and butadiene-nitrile rubber and others.

Thermomechanical curves (Figure 9) and curves of turbidimetric titration styrene and SKN-26 in a 1:1 ratio.

The character of the thermomechanical curve of the block polymer differs from that of the original components in the elastomeric deformation range belonging to the rubber, and in the viscous flow range at low stresses, peculiar to polystyrene.

For the identification of the block polymer the product obtained after processing in the modifier was fractionated from acetone solution with methanol. It was not found possible in practice to separate the product into fractions, since it precipitates almost completely in a narrow range of concentrations of the precipitant.

In Figures 10 and 11 we present the curves of turbidimetric titration of the original substances—polystyrene and rubber, the reprecipitated block polymer and the mechanical mixture of the original components.

The turbidimetric curve of the mechanical mixture (curve *2*, Figure 11) has two points of inflection, characteristic of rubber and polystyrene (rubber begins to precipitate at a 40% concentration of the precipitant, methanol), while the curve of the block polymer (curve *1*, Figure 11) has the monotonic character typical of a single-component system.

Thus a new type of polymer is produced also on the continuous modifier.

CONCLUSIONS

1. In special apparatus (a laboratory modifier and a continuous modifier) block polymers are produced from condensation resins and various starting polymers by a mechanochemical method.

2. It is demonstrated that the physicochemical properties of the resulting block polymers differ essentially from the properties of a mechanical mixture of homopolymers, which makes it possible to produce polymers with new properties.

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THE EFFECT OF ELECTRIC CHARGES FORMED DURING REPEATED DEFORMATIONS ON THE FATIGUE RESISTANCE OF VULCANIZATES*

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Electroelastic and triboelastic effects result in the formation of electric charges on articles made from polymers undergoing deformation. It was of interest to determine the effect of the charges formed during deformation on the fatigue resistance of vulcanizates. No convincing experiments clearly demonstrating the role of electric charges arising during friction or deformation had been carried out previously.

Vulcanizates containing different amounts of acetylene black were tested in a machine in which cylindrical specimens with thickened ends were subjected to repeated bending at 1300 cycles/minute.

The stocks had the following composition (in parts by weight): SKS-30A 100, sulfur 2, technical stearin 2, Rubrax 5, black oil 4, MBTS 0.6, diphenylguanidine 0.8, zinc oxide 5, oleic acid 1. Increasing amounts of acetylene black were added to this composition: 6, 12, 18, 20, 22, 30, 40 and 75 wt. parts per 100 wt. parts of rubber.

The experiments showed that specimens containing from 0 to 22 wt. parts of carbon black are nonconducting at 127 v as a network structure is not formed with these amounts of acetylene black. Vulcanizates containing 30 wt. parts of acetylene black and over are conducting. Specimens of the above composition were tested for fatigue resistance by two methods. In one method, the surface of the vulcanizate specimen was brought in contact with the conducting metal surface of the machine for repeated-deformation tests. In the other method the parts of the specimens placed in the clamps were covered with insulating caps of natural rubber.

The nonconducting specimens, containing up to 22 wt. parts of carbon black, gave the same endurance results by the two methods. The conducting specimens, containing 30 wt. parts of carbon black and over, differed considerably in fatigue endurance according to whether the charges formed could be conducted away. Thus, a specimen containing 30 wt. parts of carbon black failed after 215,000 cycles when tested with insulated ends, whereas when the charges could escape it showed no visible changes after 315,000 cycles. A specimen with 40 wt. parts of carbon black failed after ~23,000 cycles in a test with insulated ends, and after ~48,000 cycles without insulation. A specimen with 75 wt. parts of carbon black failed after 8,000 cycles in the first case, and after ~20,000 cycles in the second.

Thus, the fatigue resistance is more than doubled by the formation of conducting paths of a dispersed filler in the rubber, if the electrical charges produced during repeated deformation are conducted away.

The formation of the charges can hardly be attributed to polarization, as the bound charges formed in the polarization of dielectrics cannot be removed by the method used in these experiments.

* Reprinted from *Colloid Journal* **20**, 375 (1958); a translation by Consultants Bureau Enterprises, Inc., of *Kolloid. Zhur.* **20**, 397 and 398 (1958).

POLYMERIZATION OF ISOPRENE BY ORGANOMAGNESIUM COMPOUNDS *

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The literature contains no indication whatever concerning the possibility of polymerizing diene hydrocarbons with the aid of organomagnesium compounds. We have established, in the case of isoprene, that such a process may be accomplished at elevated temperatures employing organomagnesium materials free of ether. We have utilized butylmagnesium chloride, butylmagnesium bromide, butylmagnesium iodide, dibutylmagnesium, and the systems $(C_4H_9MgI + (C_4H_9)_2Mg)$ and $(C_6H_5MgCl + (C_6H_5)_2Mg)$, as agents for polymerization. Such systems can be obtained in the form of homogeneous solutions, utilizing organomagnesium synthesis in which the magnesium is allowed to interact directly with the halogen derivative in a hydrocarbon medium[1]. Dibutyl magnesium was obtained by quantitative separation of butyl magnesium iodide from the mixture $(C_4H_9MgI + (C_4H_9)_2Mg)$ using dioxane according to previously published methods[2]. Alkylmagnesium halides, free of ether, were synthesized by Ziegler's method[3] and used as suspensions. Each of the materials listed induced polymerization having appreciable velocity at 80–90° C.

Data are given in this paper on the polymerization at 90° C of isoprene and on the microstructure of the polymer when a monomer concentration in the solution of about 60 mole per cent (Table 1) is used. The results indicate that the polyisoprene formed by polymerization under the influence of organomagnesium compounds is distinguished by a decrease in unsaturation affiliated with a retention of complete solubility in benzene which appears to be a result of an intramolecular cyclization of the polymer chains. Another characteristic feature of these polymers is that they consist mainly of 3,4 units, connected with an appreciable increase in the glass temperature which, in our samples, ranges around −10° C; as is known, normal *cis*-1,4-polyisoprene usually has a T_g value around −70°.

Conducting the polymerizations with chloro, bromo and iodo derivatives has allowed us to establish that the nature of the halogen in the organomagnesium compound influences the relative content of the units in the polymer chain. No effect, due to the nature of the radical of the organomagnesium compound, was confirmed by detailed investigation, however in comparing the data obtained from using the butyl and the phenylmagnesium halides, it appears that the structure in each case is identical. A spectrogram of one such polymer is shown in Figure 1.

We have shown that complex-forming agents such as ethyl ether and triethylamine substantially reduce the velocity of the polymerization of isoprene, and the degree of retardation is dependent upon the concentration of these added materials (Figure 2 and Table 2).

The literature indicates that the presence of complex-forming agents in the

* Translated by J. R. Robinson from *Vysokomolekulyarnye Soedineniya*, Vol. 2, pages 541–545 (1960).

TABLE 1

POLYMERIZATION OF ISOPRENE WITH ORGANOMAGNESIUM COMPOUNDS AT 90° C IN CUMENE

(CONCENTRATION OF MONOMER: 60–65 MOLE %; SOLUBILITY IN BENZENE: 100%)

Reagent					Characteristics of polymer			
Formula	Moles	Ratio[a], agent: monomer	Polymerization time, hours	% Yield of polymer	Setting temp., °C	Unsaturation, %	[η]	3,4 links[b] in chain %
$(C_4H_9MgI+(C_4H_9)_2Mg)$[c]	0.0030	0.020	20.	28.	−9.	84.	0.82	96.
$(C_4H_9MgI+(C_4H_9)_2Mg)$[c]	0.0040	0.020	39.	41.	−3.	82.	0.95	96.
C_4H_9MgCl	0.0025	0.017	40.	29.	—	77.	0.75	99.
C_4H_9MgCl	0.0030	0.022	38.	50.	—	80.	0.70	95.
C_4H_9MgBr	0.0070	0.044	22.	20.	−12.	80.	0.84	98.
C_4H_9MgBr	0.0060	0.040	40.	35.	−7.	79.	0.81	97.
C_4H_9MgI	0.0029	0.013	43.	14.	−5.	80.	0.88	97.
C_4H_9MgI	0.0026	0.016	21.	4.	−10.	77.	0.90	98.
$(C_4H_9)_2Mg$	0.0015	0.010	44.	8.	—	30.	0.75	98.
$(C_4H_9)_2Mg$	0.0030	0.020	40.	12.	—	79.	0.78	98.
$(C_4H_9MgCl+(C_4H_9)_2Mg)$	0.0009	0.007	40.	8.	−8	83.	0.92	93.
$(C_4H_9MgCl+(C_4H_9)_2Mg)$	0.0009	0.007	35.	7.	−7	79.	0.94	—

[a] Calculations of equivalence relationships are based upon the number of individual "R" groups. Thus, in the system $(C_4H_9MgI+(C_4H_9)_2Mg)$, where the alkylmagnesium halide and the dialkyl magnesium are found in equimolecular proportions, the equivalence is calculated as $(C_4H_9MgI+(C_4H_9)_2Mg)$ divided by 3.

[b] The microstructure of the polymer is based upon infrared methods devised by E. I. Pokrovskii of the Institute for Macromolecular Compounds of the Academy of Sciences, SSSR.

[c] Figure 1 shows a spectrogram of one of the polymers.

polymerization of dienes by organometallic compounds is accompanied by definite indications of changes in the structure of the polymer chains. Similar effects have been observed with dithio-organic materials[4]. In this connection, we conducted special investigations on isoprene polymerization in the presence of ethyl ether and triethylamine, with a thorough investigation of the structure of the polymers so formed. As shown, these appear to have a noticeably diminished content of 3,4 units in the polymer chains (Table 3).

The definite lowering of the glass point of the polymers in those experiments utilizing ethyl ether is not connected with a change in microstructure of the polymer, but probably is due to an increase in the relative content of low-molecular weight polyisoprene.

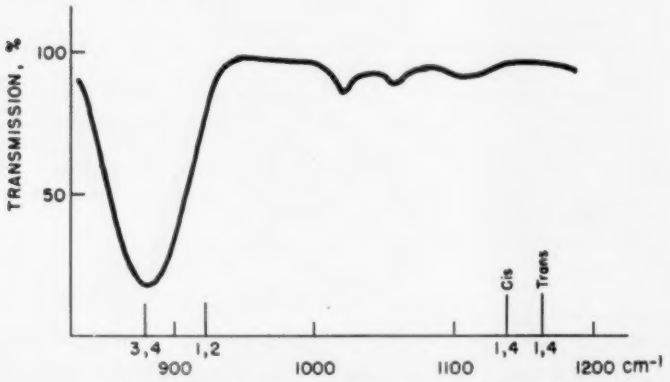

FIG. 1.—Infrared spectrum of polyisoprene in carbon disulfide.

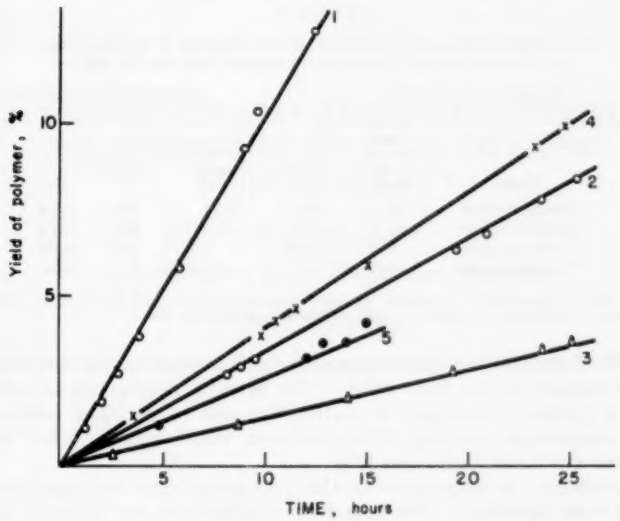

FIG. 2.—Influence of complex-forming agents on the velocity of polymerization of isoprene using $(C_4H_9MgI + (C_4H_9)_2Mg)$ at 90°. *1*—without complexing agent; *2* and *3*—with diethyl ether; *4* and *5*—with triethylamine.

EXPERIMENTAL

Synthesis of organomagnesium compounds.—For ether-free synthesis, we used a cumene solution of the organomagnesium material according to published methods[1] at 130–140° C. We have also succeeded in carrying out the reaction in paraffinic hydrocarbons. The procedure can be greatly facilitated by using instead of the usual type of apparatus for organomagnesium syntheses a sealed tube in a thermostat which is fitted with a stirring or shaking device. The following data are from a typical run: In a 250 ml ampoule was placed 15.5 g of powdered magnesium (0.65 mole) and, after twice evacuating and filling with nitrogen, there was added under a stream of nitrogen 42 g of butyl iodide (0.22 mole) and 175 ml. of solvent. The ampoule, with constant rotation, was heated at 135° for two hours. On cooling, the contents of the ampoule which were kept excluded from contact with the air, were put through a Schott filter into a Schlenk apparatus. Concentration of organomagnesium compound in solution—0.81 mole/g; overall yield—65% of theoretical. The relative content of dibutylmagnesium and butylmagnesium iodide was established by difference between the values obtained by acidimetric and argentimetric titra-

TABLE 2

RATIO OF COMPONENTS IN THE KINETIC EXPERIMENTS

Curve (in Figure 2)	Organomagnesium component, mole	Complexing Agent		Molar content of monomer in solution, %
		Name	Mole	
1	0.0026	—	—	59.2
2	0.0028	Diethyl ether	0.0056	61.9
3	0.0030	Diethyl ether	0.0150	62.5
4	0.0026	Triethylamine	0.0052	63.4
5	0.0026	Triethylamine	0.0260	59.2

TABLE 3

POLYMERIZATION OF ISOPRENE BY (C_4H_9MgI + $(C_4H_9)_2Mg$) IN PRESENCE OF COMPLEX-FORMING AGENTS AT 90°[a]

Molar conc. of monomer in solution, %	Complex-forming agent: Name	Complex-forming agent: Molar ratio to org. mag. cmpd.	Yield %	Characteristics of polymer: Setting temp. °C	Characteristics of polymer: Unsat'n %	Characteristics of polymer: [η]	Characteristics of polymer: 3,4 links in chain %
63.9	Diethyl ether	2:1	39.5	−21.1	85	0.78	86
61.7	Diethyl ether	5:1	30.9	−22.5	80	0.75	88
63.9	Triethylamine	2:1	39.0	− 7.0	79	0.92	83
48.2	Triethylamine	10:1	—	−10.0	84	0.90	86

[a] All are 48-hr. experiments. Quantity of organomagnesium compound 0.006 mole. Molar ratio, organomagnesium compound to monomer, 1:50. Solubility in benzene, 100%.

tions. The molar ratio of the components in this reaction, as well as in other runs, was usually not far from unity. The ratio of components in our second run of the system (C_6H_5MgCl + $(C_6H_5)_2Mg$) was 1:2.8. The concentration of organomagnesium material in the solution which was used for the polymerizations was 0.2–0.3 mole per liter.

Polymerization of isoprene.—In the polymerizations we used 30–50 ml ampoules with partitions. Previous to the experiment the ampoule was subjected to pre-heating *in vacuo* at 180–200° C. Monomer was subjected to careful preliminary purification, distilled from butyllithium using a chaser, into one compartment of an ampoule which, after filling, was sealed. The solution of organomagnesium compound and complex-forming agent was introduced from the Schlenk apparatus into another section of the ampoule which was also sealed. Powdered alkylmagnesium halide was introduced from a special ampoule with nitrogen flushing. At 90° the glass partitions were broken.

The polymer obtained was precipitated and washed once with methyl alcohol, then dried *in vacuo* at 40°.

Before determining structure, the viscous, unsaturated polymer was purified by double precipitations from a 2% benzene solution of methyl alcohol. The unsaturation was then assayed using iodine chloride[5].

The polymerization velocity was determined by a dilatometric method in ampoules having a graduated neck.

CONCLUSIONS

1. It was established that ether-free organomagnesium compounds promote the polymerization of isoprene at elevated temperatures.

2. The polyisoprene so-formed is mainly 3,4 linked. The nature of the halogen and radicals in the organomagnesium material has no influence on the microstructure of the polymer chains.

3. The presence of complex-forming agents (ethyl ether and triethylamine) affect an appreciable reduction in the velocity of polymerization and a marked lowering in the content of 3,4 links in the chains.

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ANALYSIS OF *CIS* AND *TRANS* 1,4 CONTENTS OF POLYISOPRENES BY NEAR INFRARED SPECTROSCOPY *

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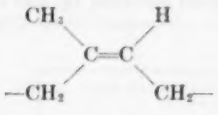
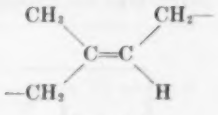
INTRODUCTION

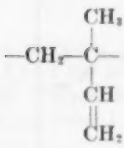
Isoprene can polymerize in four different ways to give the following repeating units:



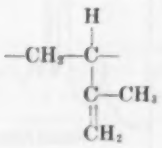
cis-1,4



trans-1,4



1,2



3,4

The last two structures may be determined using the normal infrared region but the determination of *cis* and *trans* 1,4 repeating units in mixtures of the two has proved very difficult. This has been encountered in the analysis of mixtures of gutta percha and natural rubber and also in the examination of synthetic polyisoprenes made using Ziegler-type catalysts. Various infrared methods have been tried[1] but they all failed owing to lack of reproducibility of results.

This paper describes a method for determination of *cis* and *trans* 1,4 repeating units based on the near infrared region, i.e., 1–2.8 μ, which is more accurate than that using the normal infrared region.

EXPERIMENTAL

The instrument used for qualitative and quantitative work was a Beckman model DK-2 spectrometer. The normal operating settings were as follows: scanning time, 50; scale expansion, expanded 2 ×; time constant, 0.2; sensitivity, 100. Carbon tetrachloride solutions of the polymers, approximately 1% concentration, were used and carbon tetrachloride was used in the reference beam. Fused silica or glass cells, usually 4 cm path lengths, were used.

The reference samples of natural rubber and gutta percha were specially purified to remove gel (solutions being filtered through muslin several times

* Reprinted from *Spectrochimica Acta*, 1959, pages 598–604.

and dried) and standard solutions were made up in the following manner. After weighing out the polymer (ca. 0.5 g) into a 50 ml flask, some carbon tetrachloride was added and the mixture was left overnight so that the solvent would swell the polymer. After securing the stopper of the flask (e.g., with Sellotape, transparent adhesive tape, from Gordon & Gotch Ltd., 8/10 Paul St., London E.C.2), the mixture was shaken on a laboratory wrist-action shaker for about 4 hr until the polymer dissolved. The solutions were then made up to the mark in the flasks and were ready for use.

Samples of synthetic polyisoprenes were made up in a similar manner, benzene, which interferes with the determination (see Discussion), having been completely removed. Since the synthetic polyisoprenes sometimes contained appreciable amounts of gel, which required removal by filtration, dry weight determinations on these samples were carried out, after running their spectra, by filling 10 ml flasks with the solution contained in the 4 cm cells, using a large hypodermic syringe. On evaporation of the solvent in a vacuum oven (without raising the temperature above 40° C) until the flasks reached constant weight, the percentage concentration of original solution (g/100 ml) could be calculated.

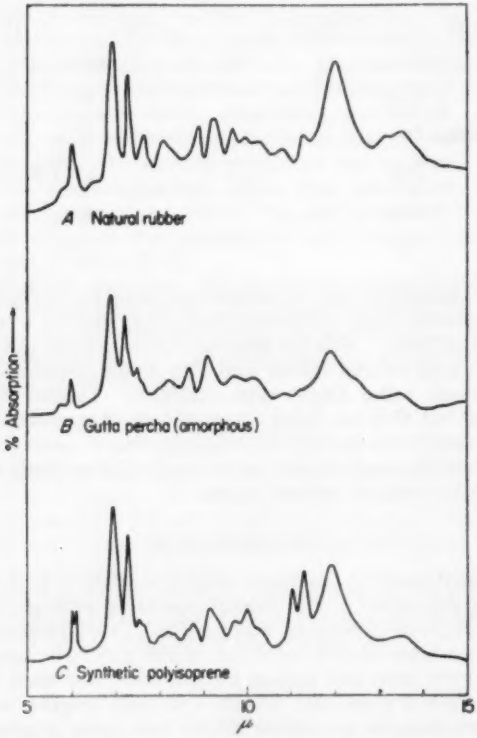


FIG. 1.—*A*. Infrared spectrum of a film of natural rubber. *B*. Infrared spectrum of a film of gutta percha in the hot cell at a temperature >73° C. *C*. Infrared spectrum of a film of a synthetic polyisoprene.

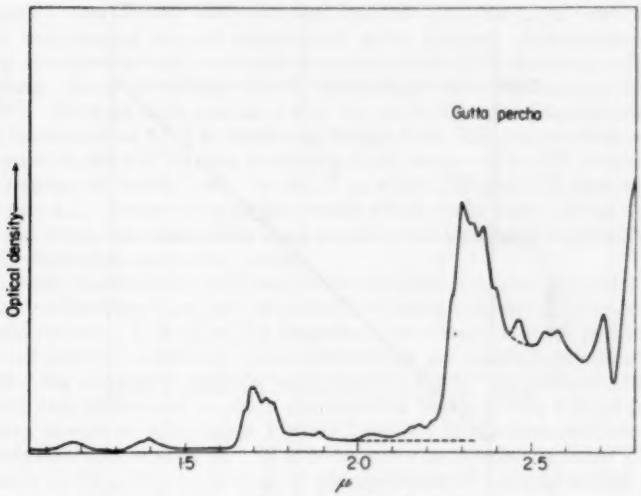


FIG. 2.—Near infrared spectrum (1.05–2.8 μ) of a ca. 1% solution of gutta percha in a 4 cm cell.

DISCUSSION

In normal infra-red spectra of polyisoprenes containing all four repeating units, the 1,2 and 3,4 additions may be distinguished and estimated by using absorptions at 910 and 890 cm^{-1}. Great difficulty arises, however, in the estimation of *cis* and *trans*-1,4 additions as the absorptions due to these components

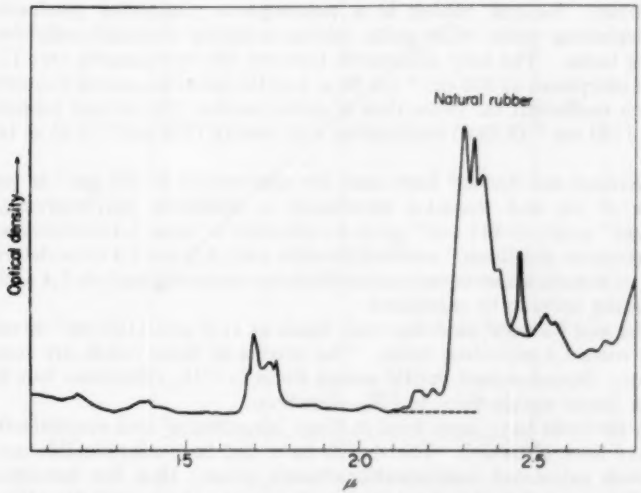


FIG. 3.—Near infrared spectrum (1.05–2.8 μ) of a ca. 1% solution of natural rubber in a 4 cm cell.

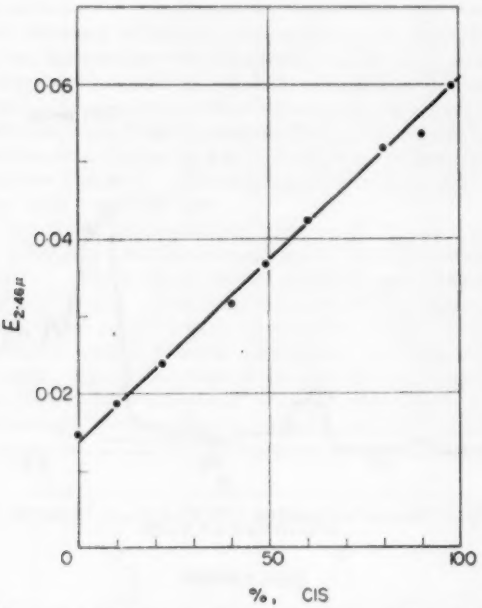


FIG. 4.—$E^{1\%}_{1cm}$ for the 2.46 μ band vs. percentage *cis*-1,4 content for synthetic mixtures of natural rubber and gutta percha.

are very similar. This is illustrated in Figure 1, which shows the infrared spectra of natural rubber, gutta percha (in the amorphous state) and a synthetic polyisoprene. Natural rubber is a polyisoprene containing predominantly *cis*-1,4 repeating units while gutta percha contains predominantly *trans*-1,4 repeating units. The only differences between the two spectra are: (1) both display absorptions at 835 cm^{-1} (11.98 μ) but the band in natural rubber has an extinction coefficient ca. twice that of gutta percha; (2) natural rubber has a band at 1130 cm^{-1} (8.85 μ) contrasting with one at 1152 cm^{-1} (8.68 μ) in gutta percha.

Richardson and Sacher[2] have used the absorptions at 835 cm^{-1} to estimate amounts of *cis* and *trans*-1,4 structures in synthetic polyisoprenes. The "crossover" point at 811 cm^{-1} gave an estimate of total 1,4-addition and the peak absorption at 835 cm^{-1} enabled the ratio *cis*-1,4/*trans*-1,4 to be determined. The use of simultaneous equations enabled the percentages of *cis*-1,4 and *trans*-1,4 repeating units to be calculated.

Binder and Ransaw[3] used the weak bands at 1130 and 1152 cm^{-1} to estimate *cis*- and *trans*-1,4 repeating units. The origins of these bands are somewhat uncertain. Saunders and Smith[4] assign them to CH_2 vibrations, but Sutherland and Jones[5] assign them to CH_3 vibrations.

Both methods have been tried in these laboratories[1] and unsatisfactory results have been obtained. The results have not been reproducible and have often given calculated concentrations much greater then the concentrations used. The near infrared region was therefore explored to see whether this would provide additional information.

Figures 2 and 3 show near infrared spectra (1.05–2.8 μ) of carbon tetrachloride solutions of natural rubber and gutta percha. Absorptions in this region of the spectrum are overtones or combinations of fundamental vibrations, particularly those involving X—H groupings, i.e., containing hydrogen atoms[6–8]. Between 2.75 and ca. 1.8 μ, the most important bands are due to binary combinations of XH stretching modes with XH deformations or combinations with other vibrations involving the X atom. The CH first overtones give a number of bands from 1.6 to 1.8 μ, while NH and OH first overtones extend to 1.4 μ. Other combination bands which occur from 1.35 to 1.5 μ and the second overtones from 1.0 to 1.2 μ require very long path lengths and have not been studied in such great detail.

The most characteristic difference between natural rubber and gutta percha is a sharp combination band at 2.46 μ which occurs in the near infrared spectrum of natural rubber. A band at this frequency also occurs in gutta percha but of very much reduced intensity. The absorptions are possibly combinations of CH stretching vibrations with the bands used by Binder[3] at 1130 and 1152 cm^{-1}. There are also differences in other combination bands in the 2.3–2.5 μ region which may be seen on referring to Figures 2 and 3. In the first overtone region, the absorption due to CH_2 at 1.72 μ is ca. twice as intense as other CH_2 and CH_3 bands (1.70 ,1.76 and 1.78 μ) in the spectrum of natural rubber; in the spectrum of gutta percha, the ratio is somewhat reduced.

In gutta percha-natural rubber mixtures and in synthetic polyisoprenes made using Ziegler-type catalysts, amounts of 1,2 and 3,4 repeating units are small and the main emphasis is on the determination of *cis*-1,4/*trans*-1,4 ratios.

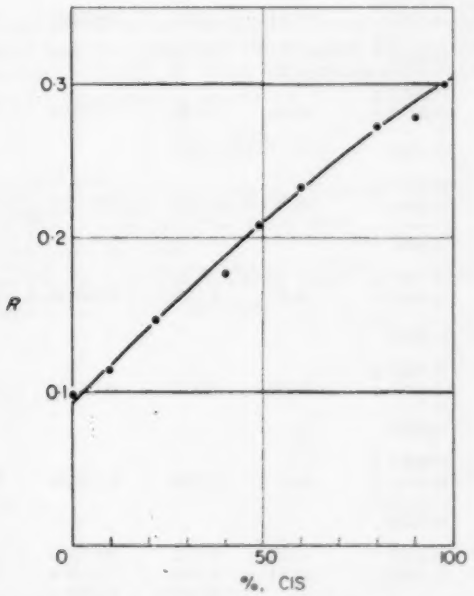


FIG. 5.—$R = (A_{1.46}/A_{1.51})$ vs. percentage *cis*-1,4 content for synthetic mixtures of natural rubber and gutta percha.

Vinyl and vinylidene groups, i.e., 1,2 and 3,4 repeating units, can, however, be estimated also by near infrared spectroscopy[1,9].

Synthetic mixtures of natural rubber and gutta percha were thus made up to see whether a method based on the 2.46 μ band could be used for *cis*-1,4/*trans*-1,4 determination. Figure 4 summarizes results obtained and plots $E^{1\%}_{1cm}$ for the 2.46 μ band against percentage *cis*-1,4-content. It was assumed for these calculations that natural rubber contains 97.8 per cent *cis*-1,4-units and gutta percha contains 98.7 per cent *trans*-1,4-units[3]. It may be seen that the results lie fairly well on a straight line and this has been used to evaluate synthetic polyisoprenes. It was verified that Beer's law held over the range of concentrations and path lengths used by carrying out several determinations using different concentrations of natural rubber and gutta percha and different path lengths.

An alternative method which does not involve dry weight determinations is shown in Figure 5. This uses the band at ca. 2.315 μ as a thickness standard, as

TABLE I

Polymer	Concn. (g/50 ml)	*cis* (%)	$A_{2.46\mu}$	$E^{1\%}_{1cm}$	$A_{2.31\mu}$	$\frac{A_{2.46\mu}}{A_{2.31\mu}}$
Gutta percha	0.5099	(98.69 trans)	0.060	0.01471	0.615	0.0975
Gutta-natural rubber	0.4515 g 0.0496 c	9.82	0.075	0.01871	0.656	0.1143
	0.5011					
Gutta-natural rubber	0.4019 g 0.1134 c	21.84	0.099	0.02402	0.674	0.1469
	0.5153					
Gutta-natural rubber	0.2982 g 0.2012 c	40.06	0.126	0.03154	0.716	0.1760
	0.4994					
Gutta-natural rubber	0.2533 g 0.2464 c	49.07	0.147	0.03677	0.707	0.2079
	0.4997					
Gutta-natural rubber	0.1987 g 0.3005 c	59.97	0.169	0.04232	0.727	0.2325
	0.4992					
Gutta-natural rubber	0.1021 g 0.4084 c	79.85	0.212	0.05191	0.780	0.2718
	0.5105					
Gutta-natural rubber	0.0503 g 0.4631 c	90.1	0.220	0.05356	0.790	0.2784
	0.5134					
Natural rubber	0.5059	97.78	0.242	0.05979	0.808	0.2995
Ameripol SN	0.2865	96.8†	0.136 0.336*	0.05934 0.05864	0.482	0.2822

* 10 cm cell.
† From calibration chart, Figure 4.

it does not vary very much in intensity on going from gutta percha to natural rubber using synthetic mixtures. The ratio $R = A_{2.46\mu}/A_{2.315\mu}$ is plotted against percentage *cis*-1,4 content. This method has the advantage that it could be applied to determinations on films as well as solutions. Typical base lines used for these determinations are shown in Figures 2 and 3. *N.B.* If benzene is present even in small amounts, it interferes with the determination as it has a very strong absorption at 2.46 μ.

RESULTS

Table I lists data and results obtained for natural rubber, gutta percha and synthetic mixtures as well as some for synthetic polyisoprenes. Ameripol SN which was reported[10] to be a "synthetic natural rubber" by Goodrich-Gulf Corp. is shown to have a high *cis* content, very akin to natural rubber.

The substance of this paper has already been described at the joint meeting of the Infrared Discussion Group and the Photoelectric Spectroscopy Group held at King's College, London, on 2 January 1959.

SUMMARY

A new method for the determination of *cis* and *trans*-1,4 units in synthetic polyisoprenes and gutta-rubber mixtures has been developed. The method uses the near infrared region of the spectrum and gives better, more reproducible results than the one using the normal infrared region.

ACKNOWLEDGMENT

This work was carried out in the Central Research Division of the Dunlop Rubber Company and the Directors are thanked for permission to publish. Thanks are also due to Mrs. B. H. Wood for running some of the spectra and to Mr. C. G. Baker for experimental assistance.

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ABSENCE OF 3,4-STRUCTURE IN NATURAL POLYISOPRENES *

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The concentration of 3,4 structure in hevea and balata has been the subject of some controversy in the past few years. The controversy concerns the assignment given to an absorption band found at 11.25 μ in the spectra of hevea and balata. It is known from the spectra of simple compounds that the isopropenyl group gives an absorption band at 11.25 μ, and that an absorption occurs at 11.25 μ in the spectra of synthetic 3,4(isopropenyl)-type polyisoprene. Salomon and van der Schee[1], in 1954, stated that it was tempting to assign the 11.25 μ peak in hevea and balata to the 3,4-type structure; however, they found that the absorption at 11.25 μ survived ozonization of the polymer. This cast some doubt on the validity of the assignment. Binder[2], in 1957, assigned the absorption at 11.25 μ to 3,4 structure and calculated that hevea and balata contained 2.2 and 1.3 wt-% 3,4 structure, respectively.

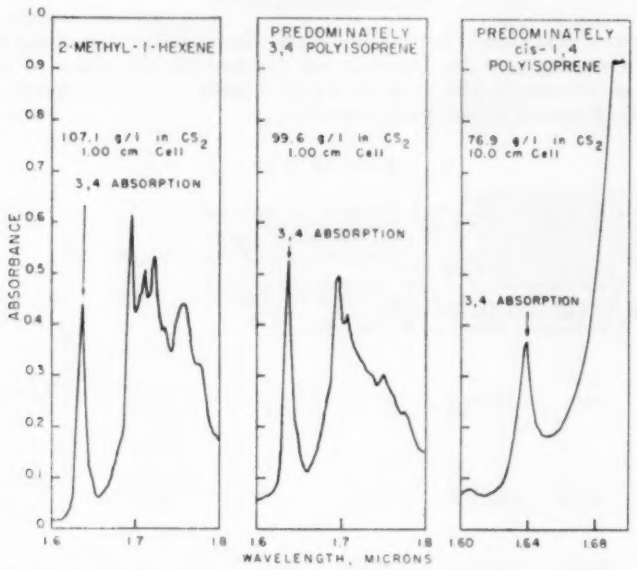

FIG. 1.—Near-infrared spectra of 3,4 structure in 2-methyl-1-hexene, a predominantly 3,4-polyisoprene, and a predominantly cis-1,4-polyisoprene.

* Reprinted from the *Journal of Polymer Science* **41**, 522–524 (1959).

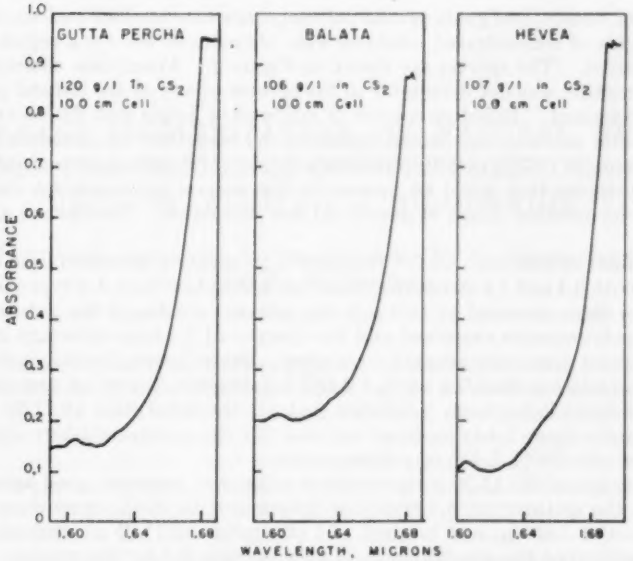

FIG. 2.—Near-infrared spectra of natural polyisoprenes.

An investigation of the near-infrared absorption of 3,4-type structures has been made. As a result of this study, spectroscopic evidence has been obtained to support the assumption that hevea and balata are 100% 1,4-type polyisoprenes.

The absorption of radiation in the 1.6 μ region of the near-infrared by compounds containing the terminal vinyl group is well established[3]. The absorption results from the first overtone of the carbon-hydrogen stretching vibrations of the $=C=CH_2$ structure. Both vinyl- and isopropenyl-type groups contain this structure and simple olefins of both the 1,2 or 3,4 type absorb near 1.6 μ in the near-infrared. The spectrum of 2-methyl-1-hexene, a simple 3,4 olefin, is shown in Figure 1. The characteristic 3,4 absorption is found at 1.638 μ. The near-infrared absorption of polymeric 3,4 structure was determined from near-infrared spectra of (*1*) a synthetic polyisoprene containing about 70 wt-% 3,4 structure and (*2*) synthetic *cis*-1,4-polyisoprenes containing between 1 and 10 wt-% 3,4 structure. The absorption characteristic of polymeric 3,4 structure is found at 1.649 μ as shown in Figure 1. The absorptivity of polymeric 3,4 structure was calculated to be 0.35 l/mole cm which compares quite closely with the 0.37 l/mole cm absorptivity of 3,4 structure in simple olefins.

TABLE I

LIMIT OF DETECTION OF 3,4-STRUCTURE IN NATURAL POLYISOPRENES

Polyisoprene	Concentration, g/l	Absorbance at 1.639 μ	Limit of detection for 3,4 structure, wt-%
Hevea	107	<0.01	<0.2
Balata	106	<0.01	<0.2
Gutta percha	120	<0.01	<0.2

Hevea, balata, and gutta percha polyisoprenes were purified and the absorption spectra of concentrated solutions were obtained in the 1.6 μ region of the near-infrared. The spectra are shown in Figure 2. Absorption characteristic of 3,4 structure was not detectable in the spectra of any of the natural polyisoprenes examined. Based on spectra of mixtures of balata and known amounts of synthetic polyisoprene, which contained 3,4 structure, an absorbance from 3,4 structure at 1.639 μ of 0.01 units is detectable. The maximum concentration of 3,4 structure that could be present in the natural polyisoprenes examined and not be detected (limit of detection) was calculated. Results are given in Table I.

The limit of detection for 3,4 structure is in reality a detection limit for the total of both 3,4 and 1,2 structures; however, absorption from 1,2-type structure has never been observed at 11.0 μ in the infrared spectra of the naturally occurring polyisoprenes examined and the absence of 1,2-type structure in these polyisoprenes has been generally accepted. Since hevea, balata, and gutta percha contain less than 0.2 wt-% 1,2 and 3,4 structure (based on near-infrared measurements) it has been concluded that (*1*) the absorption at 11.25 μ does not originate from 3,4-type structure, and (*2*) the natural rubbers examined are essentially 100% 1,4-type polyisoprenes.

The origin of the 11.25 μ absorption is unknown; however, good agreement between the quantity of 3,4 structure determined by both near-infrared (3,4 absorption at 1.639 μ) and infrared (3,4 absorption at 11.25 μ) methods is obtained only when the absorption at 11.25 μ is corrected for the presence of the non-3,4 absorption. The results strongly suggest that the absorption at 11.25 μ in hevea, which does not originate from 3,4 structure, is not unique to hevea but persists in the spectra of predominately *cis*-1,4-type synthetic polyisoprenes.

ACKNOWLEDGMENT

The author wishes to express his gratitude to Dr. R. J. Ehrig for the preparation of several synthetic polyisoprenes used in this study.

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CIS-TRANS ISOMERIZATION OF NATURAL RUBBER UNDER THE INFLUENCE OF HYDROGEN CHLORIDE OR ETHYLALUMINUM DICHLORIDE *

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Lebedev Scientific Institute for Synthetic Rubber, Leningrad, USSR

We have established earlier that organo-aluminum compounds, and titanium tetrachloride, bring about the isomerization[1] of the *cis*-isoprene units in natural rubber into the *trans*. The isomerization process, as influenced by the above materials, proceeds at appreciable velocity even at room temperature. The present communication reports the results of investigating the *cis-trans* isomerism of natural rubber as influenced by hydrogen chloride and ethylaluminum dichloride. The isomerizing action of hydrogen chloride upon unsaturated acids and stilbene was dislosed earlier in a series of papers[2–7].

We investigated the action of dry hydrogen chloride and ethylaluminum dichloride on benzene solutions of natural rubber under the conditions described earlier[1]. Hydrogen chloride was introduced in the form of a saturated benzene solution. In investigating the hydrogen chloride activity, each polymer sample was examined for unsaturation, chlorine content of the polymer chains and microstructure. The latter was characterized with the aid of infrared absorption spectra. As in the previous report[1], quantitative determination of the *cis* and *trans* content was made in the 840 cm^{-1} region, where the intensity and contour are substantially dissimilar for natural rubber and guttapercha. Furthermore, an additional inspection was made qualitatively in other regions of the IR spectrum (1100–1150 cm^{-1} and 1300–1330 cm^{-1}), the feasibility of utilizing the 1300–1330 cm^{-1} region having been reported in a recent publication by Golub[9], who investigated the isomerization of natural rubber and guttapercha under the influence of selenium at temperatures of 180–220°.

In connection with the fractional decrease in unsaturation of the polymer due to addition of HCl, the relative content of units of one or the other configuration was computed as a percentage of the residual double bond content of the polymer.

Results of the experimental work are summarized in Table I, and in Figures 1 and 2. It should be noted that assessment of the data according to the relative content of *cis-trans* links presents only a qualitative picture of the process because, in connection with decreasing unsaturation of the polymer, the precision of spectroscopic definition decreases markedly. Regarding the organic solution of the polymer, it is not always pointed out that it is possible to compensate for the decrease in double bonds by a corresponding increase in the concentration of the polymer solution under study. As the data in Table I show, ethylaluminum dichloride and hydrogen chloride effect isomerization in the polymer chain of natural rubber, in which the number of *trans* units increases with increasing concentration of the isomerizing agent.

* Translated by J. R. Robinson from *Doklady Akad. Nauk* S.S.S.R. **131**(4), 830–832 (1960).

TABLE I

ISOMERIZATION OF A 2% SOLUTION OF NATURAL RUBBER IN BENZENE

Catalyst	Wt. % of cat. in polymer	Temp., °C	Duration, hours	Structure of isoprene units, %			
				1,4-*cis*	1,4-*trans*	3,4	1,2
$Al(C_2H_5)Cl_2$	1.0	30	10	91	8	1	1
$Al(C_2H_5)Cl_2$	1.0	90	10	85	14	1	0
$Al(C_2H_5)Cl_2$	5.0	30	10	75	24	1	0
$Al(C_2H_5)Cl_2$	5.0	90	10	28	65	4	0
HCl (dry)	10.0	80	15	72	26	1	1
HCl (dry)	50.0	80	15	19	78	1	1
HCl (dry)	100.0	80	15	0	98	1	1

In both cases the process of isomerization is accompanied by a significant decrease in the unsaturation of the polymer chain. With ethylaluminum dichloride, which appears to be an effective catalyst of the cationic type in the process of polymerization, a decrease in unsaturation, obviously, is basically tied in with the process of intramolecular cyclization[8].

In the case of hydrogen chloride, the decrease in unsaturation appears due merely to the addition of HCl to the double bonds, as illustrated by the data of Figure 1. The content of HCl added corresponds to the decreased unsaturation.

With increasing duration of the experiment, there is a constant diminishing

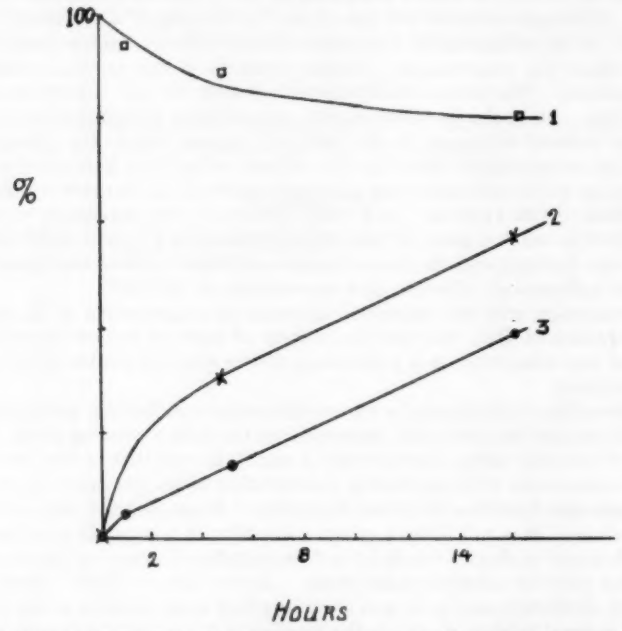

FIG. 1.—Degree of isomerization of polymer during addition of HCl as affected by duration of experiment at 30° for a weight ratio of HCl:rubber = 1. *1*—Theoretical double bond content (%); *2*—Amount of *trans*-form, expressed as a percentage of residual double bond content; *3*—Amount of added HCl as a percentage of theoretical.

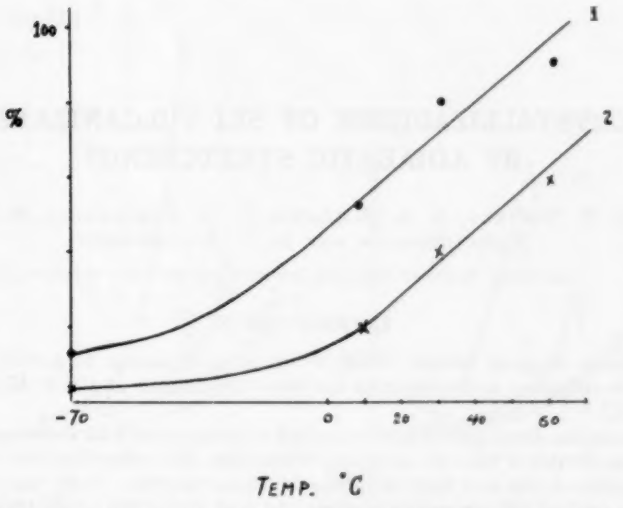

FIG. 2.—The effect of temperature on the process of isomerization of polymer on the addition of hydrogen chloride. Duration of the experiment = 5 hours. Weight ratio of HCl:rubber = 1. *1*—The number of *trans* units as a percentage of the residual unsaturation; *2*—Chlorine content of polymer.

of unsaturation (curve 1, Figure 1), an increase in the relative content of *trans*-units (curves *2* and *3*) accompanied by a constant increase in the chlorine content of the polymer (curve *3*). As seen from Figure 2, the isomerization and HCl addition processes take place even at a temperature of −70° and markedly accelerate as temperature rises. At +60° the total content of double bonds and of chlorine addition is only 82% of the theroretical value which obviously is dependent upon the development of cyclization processes.

The determinations of the *cis-trans* isomerization of the units and the content of hydrogen chloride were carried out in accordance with the schemes for these processes as published earlier[1].

Other experiments of ours have shown that, under similar conditions, *cis*-polybutadiene is not markedly isomerized. The high susceptibility of *cis*-polyisoprene to isomerization under the influence of ionic catalysts probably occurs in connection with the isostructure of the ioprene units. This is established also by the fact that stereospecific synthesis of *cis*-polyisoprene is accomplished significantly more easily than *cis*-polybutadiene.

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CRYSTALLIZABILITY OF SKI VULCANIZATES BY ADIABATIC STRETCHING*

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INTRODUCTION

Lithium isoprene rubber (SKI) which is very similar to natural rubber (NK) in structure and properties has been synthesized at the S. V. Lebedev VNIISK[1, 2, 3].

During the development of the method of preparation and the investigation of the properties of SKI the necessity of studying the crystallizability of different samples of this new type of rubber became apparent. With this object in view we studied the conversion of work into heat during the adiabatic deformation of rubbers[4]. It was shown that the conditions of preparation and of vulcanization determine whether SKI rubbers will crystallize on stretching or remain amorphous[5].

This paper presents some of our data on the crystallizability of SKI rubber.

METHOD

Two samples of SKI synthesized in a pilot plant installation were studied. For stabilization of these rubbers, 2 parts of PBNA per 100 parts of polymer were introduced on the mill. The intrinsic viscosities of these rubbers were $[\eta] = 4.7$ (SKI-4.7) and $[\eta] = 1.8$ (SKI-1.8). For comparison, a sample of milled smoked sheet (NK) having an intrinsic viscosity $[\eta] = 2.3$ was used. From all of these rubbers compounds were prepared having the following composition by weight: rubber 100, sulfur 1, DPG 3, MBTS 0.6, zinc oxide 5, stearic acid 1. Vulcanization was carried out at 134°. The apparatus used for adiabatic stretching of rubber as well as the method of measurement and calculation of results has been described elsewhere[6, 7]. The rate of extension was about 100% per second. The experiments were carried out at room temperature on samples that were not exposed to deformation prior to the test.

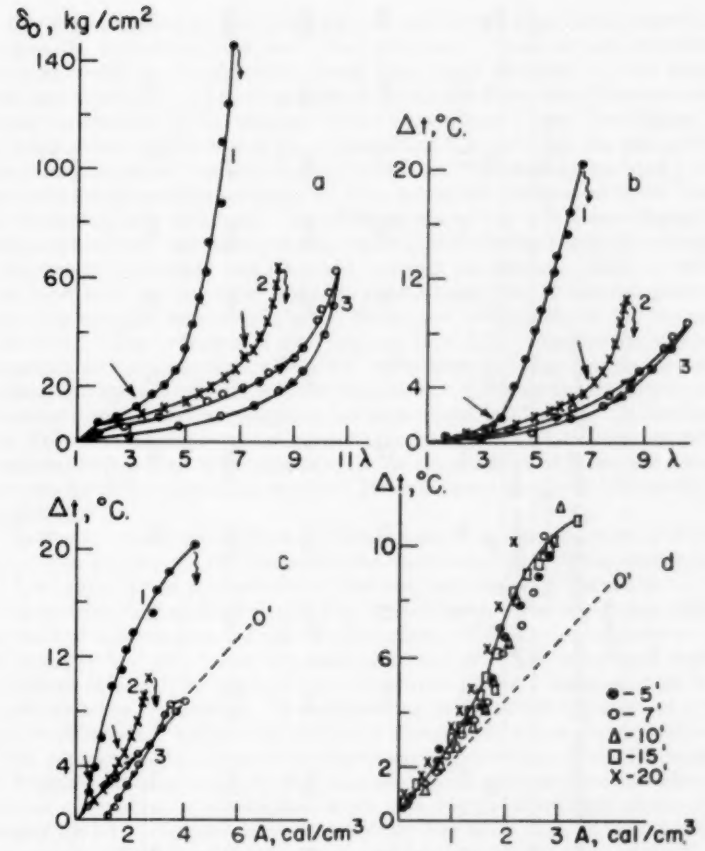
EXPERIMENTAL DATA AND DISCUSSION

Figures *a*, *b*, and *c* show experimental data for the samples of SKI and NK compounds vulcanized for 10 and 15 minutes respectively. These data are expressed in the form of the functions:

$$\delta_0 = f_4(\lambda), \quad \Delta t = f_4(\lambda), \quad \Delta t = f(A),$$

where δ_0 is the nominal stress (referred to the original cross section of the sample) in kg/cm^2, $\lambda = l/l_0$ is the degree of elongation of the uniform portion of

* Translated by Theodor Tarasjuk, Katherine and Willard P. Tyler for Rubber Chemistry and Technology from *Vysokomolekularnye Soedineniya* 1, 1016–1020 (1959).



FIGS. *a, b, c, d.*—Adiabatic deformation of compounds of natural rubber (1) and lithium isoprene rubbers SKI-4.7 (2) and SKI-1.8 (3) at 20°. *a*—Stress-strain diagram; *b*—Heating as function of stretching; *c*—Heating as a function of work of deformation; *d*—Heating of SKI-4.7 compounds differing from each other by the time of vulcanization. The legend shows the time of vulcanization in min. Arrows show the beginning of crystallization on stretching. *a*. Abscissa, λ; Ordinate; δ_0, kg/cm²; *b*. Abscissa, λ; Ordinate, Δt; *c*. Abscissa; *A*, cal/cm³; Ordinate, Δt; *d*. Abscissa, ordinate; same as for *c*.

the sample; Δt is the change in temperature in ° C; A is the specific work of deformation, cal/cm³. For comparison, Table I lists the results of the standard tests on these rubber compounds.

From Table I it can be seen that as reported in the literature[2], the SKI vulcanizates possess a lower modulus (stress, δ_0, corresponding to 300 and 500% elongation; $\lambda = 4$ and $\lambda = 6$) than the NK vulcanizates. A study of the stress-strain diagram (Figure *a*) leads to the same conclusion. At $\lambda = 4$ (300% elongation), $\delta_0 \simeq 10$ kg/cm² for SKI-4.7, while it is more than twice as great, $\delta_0 \simeq 20$ kg/cm², for NK. The SKI-1.8 compounds possess an even lower modulus than SKI-4.7. SKI vulcanizates are characterized by high extensibility and by a smooth increase in strain with applied stress. This is especially characteristic of SKI-1.8 rubber vulcanizates.

TABLE I

RESULTS OF STANDARD PHYSICAL TESTS ON RUBBER COMPOUNDS

Property	SKI, [η] = 4.7					SKI, [η] = 1.8					NK, [η] = 2.3				
	Time of vulcanization, min.														
	5	7	10	15	20	5	7	10	15	20	5	7	10	15	20
Modulus, 300%, kg/cm²	10	10	9	10	9	11	8	8	8	8	12	14	14	17	—
Modulus, 500%, kg/cm²	13	15	15	17	16	16	11	12	12	13	28	35	37	45	35
Tensile strength, kg/cm²	277	287	303	198	293	167	184	217	214	201	289	306	289	312	308
Relative elongation, %	1303	1293	1232	1146	1262	1342	1240	1305	1300	1250	908	887	836	816	868
Residual elongation, %	12	12	9	8	11	22	19	22	22	21	10	10	9	12	10

For NK compounds, $\delta_0 \simeq 145$ kg/cm² and $\lambda \simeq 6.8$ at break; for SKI-4.7 compounds, $\delta_0 \simeq 65$ kg/cm² and $\lambda \simeq 8$ at break. These values of stress and strain at break are considerably lower than those obtained by the standard tests (see Table I). The disagreement is explained by the differences in the testing conditions: (a) the samples were of complicated form (two layers), and the total cross section was high, approaching 0.4 cm²; (b) the samples were tested in a twisted (half-revolution) condition; (c) during the study of the thermoelastic properties the samples were hot at the moment of break because the stretching was adiabatic. In addition stretching was accomplished with considerable speed (250 mm per sec), while in the standard tests the elongation is practically isothermal and its speed is 8 mm per second. SKI-1.8 vulcanizates have such low modulus and high extensibility that it was not possible to break the samples at the maximum elongation obtainable on our apparatus ($\lambda \simeq 10.5$). The branches of the diagram, $\delta_0 = f_4(\lambda)$, representing stress and relaxation do not coincide for SKI-1.8. The loss of energy in this mechanical deformation cycle is about 1 cal/cm³ (Figure *c*). Data on the evolution of heat of rubber compounds on elongation are reproduced in Figure *b*. It can be seen that SKI-4.7 rubber compounds heat up more than SKI-1.8 compounds but considerably less than NK compounds. At the moment of break the temperature rise for NK compounds is about 20° compared to about 11° for SKI-4.7 compounds.

In Figure *c* the thermal effect is plotted against the specific work of deformation. The broken line 00′ represents the heat rise of amorphous rubber having the heat capacity of smoked sheet, 0.45 cal/cm³/degree. For all the rubbers it can be seen that at the beginning of stretching the heat rise is equivalent to the work of deformation. From the deviation of the experimental curves from the straight line 00′ it can be concluded that the NK compound starts to crystallize at $\lambda = 3$ to 3.5 and the vulcanized SKI-4.7 compound at $\lambda = 7$, about twice the elongation. It is interesting to note that the start of crystallization of SKI-4.7 compounds occurs at elongations where the crystallization of NK compounds has already decreased and degeneration of elastic properties has begun[8]. If one judges by the amount of heat evolved over and above the thermal equivalent of mechanical work, the degree of crystallization of vulcanized SKI-4.7 compounds is considerably less than that of vulcanized NK compounds. This is evidently due to the less regular structure of SKI. The SKI-4.7 compound was destroyed before reaching the elongations at which limitations in the mobility of macromolecules resulting from crystallization and orientation begin to develop.

Apparently at the high elongations at break ($\lambda = 13$–14) characteristic of SKI compounds under standard conditions, there is less difference in the degree of crystallization of SKI and NK compounds. Perhaps this is why their tensile strengths are almost equal ($\delta_0 \simeq 300$ kg/cm², see Table I). By calculation on the basis of the true original cross section the actual tensile strength of SKI vulcanizates is even higher than that of NK vulcanizates[2].

Crystallization increases the stiffness of the rubber compounds. On examination of the functions plotted in Figures *a*, *b* and *c* it is observed that at the start of the rapid rise of stress, δ_0, and the temperature rise of the specimen, Δt, coincide with the beginning of crystallization in NK and SKI-4.7 compounds, a similar occurrence has been previously noticed[9]. These points are indicated for each rubber by arrows. Changing the time of vulcanization of a given compound from 5 to 20 minutes does not appreciably change the stiffness of SKI-4.7 compounds, as seen from Table I, or their crystallizability. From

Figure *d*, representing the function $\Delta t = f_4(A)$, it can be seen that the start of crystallization of all the SKI-4.7 compounds in this series occurs at approximately the same value of speciffic work. The processes of crystallization proceed at practically the same rate with no sign of diminution on stretching up to break except for the compound vulcanized for 15 minutes, for which a decrease in the rate of crystallization can be noticed before break. It is also noticed that the same sample has lower tensile strength and elasticity than the other compounds in the series. At the same time, the SKI rubber of lower molecular weight, SKI-1.8, does not crystallize at the limiting elongation we achieve, $\lambda \simeq 10.5$. From these data it can not be categorically stated that this rubber will not crystallize. Evidently the structure of SKI-1.8 is such that elongations greater than $\lambda \simeq 10.5$ are required for crystallization. It is possible that in the standard tests (λ = 12–14, $\delta_0 \simeq 200$ kg/cm^2, see Table I) crystallization has occurred. The high strength characteristics of SKI compounds may be determined not only by their ability to crystallize only at high elongation, but by the possibility of high orientation of molecular chains under these conditions.

It can be concluded from examination of the function $\Delta t = f_4(A)$ that the coincidence of the curve for SKI-4.7 up to $\lambda < 7$ and of the SKI-1.8 curve up to $\lambda \simeq 10.5$ with the line 00′ indicates that the value of the heat capacity of SKI in the amorphous state is close to that of NK (0.45 cal/cm^3/degree). The fact that the points of the function $\Delta t = f_4(A)$ for SKI-1.8 do not lie on the line 00′ (Figure *c*) toward the end of the relaxation cycle means that during a full cycle of deformation heat was lost to the surroundings. This was not large and caused a cooling not exceeding 2° at the end of the cycle. Recognition of this error does not change the characteristics of the function $\Delta t = f_4(A)$ or the conclusions.

SYNOPSIS

The basic relationships in the conversion of work into heat during the stretching of unfilled lithium isoprene rubber (SKI) compounds were investigated. The rubber specimens examined differed in the molecular weight of the raw rubber and in the conditions of vulcanization. Vulcanizates of SKI having an intrinsic viscosity $[\eta] = 1.8$ remain amorphous on stretching to $\lambda \simeq 10.8$ while compounds of rubber with higher molecular weight ($[\eta] = 4.7$) begin to crystallize at $\lambda \simeq 7$. The degree of crystallization of SKI is less then that of natural rubber in compounds of the same composition. The latter begins to crystallize at considerably lower elongations ($\lambda \simeq 3$).

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UNPAIRED ELECTRONS IN CARBON BLACKS *

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INTRODUCTION

Unpaired electrons have been found by electron spin resonance in a number of carbons of different origin[1–7]. Low temperature carbons prepared by charring organic matter below 600° C exhibit a single resonance line which disappears upon heat treating at temperatures above 1000° C[1,4,6]. Upon further heat treatment of such carbons, a resonance reappears beyond 1400° C which is similar to that found in graphite[1,2]. No resonances have been reported for materials charred in the temperature range of 1000 to 1400° C.

Colloidal carbon blacks are prepared by rapid pyrolysis of natural gas or oils. This material differs considerably from the charred materials mentioned above. The temperature of formation of carbon blacks is 1100 to 1750° C, the reaction time is very short, and the particle size is of colloidal dimensions. These carbons are of great technological importance in the rubber, plastics, paint, and ink industries. The possibility that these carbons contain free radicals on the surface has been subject of speculation for the last few years, primarily because such free radicals might be expected to affect materially the reinforcement of high polymers, in particular elastomers, and possibly their resistance to oxidative attack. Because of the differences in pyrolysis conditions under which carbon blacks are formed, previous electron spin resonance work offered no clue to the type of free radical activity, if any, to be expected.

The present report is largely devoted to an investigation of the electron spin resonance of typical colloidal channel black (Spheron 6 manufactured by Godfrey L. Cabot, Inc.), and the carbons derived from it by heat treatment at temperatures from 500 to 3000° C. Considerable information has already been published on this series of blacks, based on x-ray diffraction, adsorption, and other techniques[8], and this information has materially aided the interpretation of the electron spin resonance data. Electron spin resonance data have also been obtained for a number of commercial carbon blacks.

EXPERIMENTAL

SPECTROMETER

The electron spin resonance spectrometer is of conventional design. Severe noise problems of the microwave assembly, caused by building vibrations, necessitated the use of a spring-supported platform from which the microwave components are suspended. The sample is placed at the center of a TE_{102} transmission cavity positioned between the poles of the electromagnet. The microwave source is a klystron operating near 10,000 Mc/sec. In addition to a slow variation for scanning purposes, the magnetic field is modulated at 15 cps

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to permit the use of phase-sensitive detection. The sensitivity is such that 0.07 cc of 5×10^{-5} molar α,α-diphenyl-β-picryl hydrazyl (DPPH) in benzene gives a signal/noise ratio of about three. A bridge-type modification of the spectrometer was made to permit one group of samples to be measured at −189° C. This arrangement was made necessary by the need for a single-ended probe which could be cooled in a Dewar within the magnetic field.

MEASUREMENT TECHNIQUES

The information obtainable experimentally from electron spin resonance spectroscopy includes line width, saturation behavior, electron spin concentration, and "g" factor. The line width as used here is the width (in gauss) between inflection points on the absorption curve. The bell-shaped absorption curve is converted to approximately the first derivative in the phase-sensitive detection method. The line width corresponds to the distance between maximum positive and negative excursions of the recorded curve. The broadening effect of the modulation amplitude is avoided by extrapolation of the measured line width to zero modulation amplitude[9].

Quantitative spin assay is a subtle problem. With identical experimental conditions, the number of spins in an unknown sample may be obtained by direct comparison with a sample of known concentration. The quantity which measures the number of spins is the area beneath the absorption curve, or, in the case of phase-sensitive presentation, the first moment divided by the modulation amplitude[10]. The factors which must be the same, or for which correction must be made, are (1) sample geometry, since the sensitivity varies throughout the cavity; (2) modulation amplitude; (3) power level, which nonetheless must not cause saturation; (4) amplifier gain; (5) klystron power output; and (6) degradation of cavity Q by the sample.

The sample geometry has not proved troublesome in that a solution of DPPH in benzene was made up in appropriate concentration to fill the same size sample tube used for the carbon blacks. The modulation setting was left untouched between runs on the carbon black and DPPH solution. The power level was adjusted to prevent saturation for each sample and, in addition, also served as a well-calibrated gain control (for power levels below saturation). Saturation measurements were needed in order that other measurements could be made in a region of linear response. The amplifier gain was stabilized by inverse feedback, by using regulated power supplies, and by allowing adequate warmup of the equipment. Power output and frequency stability of the klystron were attained by well-regulated power supplies and by immersion of the klystron in silicone oil to avoid temperature fluctuations.

The extent of degradation of cavity Q proved the most troublesome problem. Very small samples could have been used, since they do not degrade the cavity Q, but the signal/noise ratio suffers. The sensitivity of the spectrometer is proportional to the power level at the sample. This is proportional to the cavity Q, and it is evident that large errors in the assay may occur unless this factor is measured and a suitable correction is made. The method of measurement of the extent of degradation of cavity Q utilized here depends upon an otherwise undesirable effect, the "cavity resonance," which occurs in the empty cavity and is broadly at its maximum in the magnetic field region of interest. The resonance is undesirable because it leads to a tilted baseline upon which the desired resonances are observed. It is apparently caused by traces of ferromagnetic impurities on the cavity walls, since a fivefold reduction

of its intensity resulted from immersion for one hour in cold dilute HCl. The intensity of this cavity resonance was used to measure the degradation of cavity Q by each sample. With the magnetic field removed 400 gauss below that which causes resonance in organic free radicals, the cavity resonance was still near maximum deflection. This deflection decreased upon insertion of the samples, and the relative sensitivity of the spectrometer for each sample was measured directly by the cavity resonance deflection. The magntidue of this correction averaged about 1.7 for the size samples chosen, but was as large as 5 on some carbon black samples of low resistivity. The cavity resonance saturated at higher power levels, as did most of the other resonances, and a saturation run was made to establish the operating power at a sufficiently low level.

The spin concentration S (in spins per gram), was calculated from the equation,

$$S = M_1 S_0 L_0 \text{ antilog } (\langle \text{db} \rangle / 10) / M_0 L_0 m_1$$

where M_1 is the first moment of the resonance curve of the unknown, M_0 is the first moment of the resonance curve of the standard solution of DPPH (generally 0.0204 molar), S_0 is the number of spins in that portion of the DPPH sample within the cavity, $\langle \text{db} \rangle$ is the difference between the db attenuation settings at which the known and unknown samples were measured, L_0 and L_1 are the deflections of the cavity resonance with the known and the unknown samples inserted, and m_1 is the mass in grams of the unknown sample in the 0.900 in. within the cavity.

The g factor is defined as[11]

$$g = h\nu/\beta H,$$

where h is Planck's constant, ν is the microwave frequency, β is the Bohr

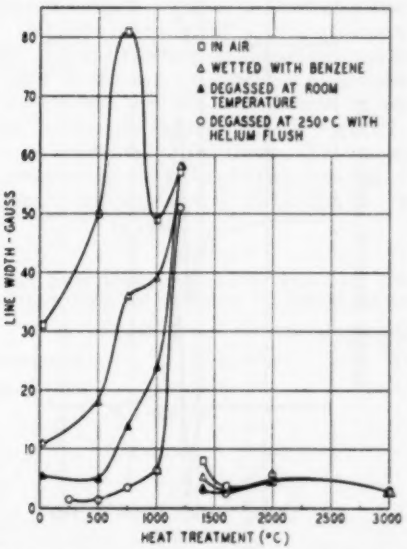

FIG. 1.—Width of electron spin resonance line in heat treated channel black.

magneton, and H is the magnetic field at the center of the resonance. The g factors were measured by alternately scanning the unknown sample and a small amount of polycrystalline DPPH whose g factor is known[12] to be 2.0036. The cavity was not tuned and the changes of its resonant frequency with each sample insertion required that the klystron be retuned. The change of frequency, $\Delta\nu$, was measured with a cavity wave meter. The change of field at resonance, ΔH, between known and unknown was determined from the change of position of the center of the resonance on the record. The change of g factor between the known and unknown, Δg, was then calculated as

$$\Delta g/g = \Delta\nu/\nu - \Delta H/H.$$

SAMPLE PREPARATION

The heat treatment (HT) of the channel black samples, which consisted of heating the sample to the specified temperature for two hours in a nonoxidizing atmosphere in an induction furnace, had been carried out elsewhere[8]. The samples were placed in glass "melting point" tubes of approximately 1 mm i.d., and were filled to a length of about 1.5 inch. This was adequate to ensure that the 0.9 inch sensitive region inside the cavity was filled regardless of positioning errors. The amount of sample within the cavity was about 0.015 g, which was the best compromise between the increase of signal/noise afforded by large samples and the ease of correction for cavity Q degradation offered by small samples. The carbon blacks had been originally formed into pellets of about 0.6 mm diam. In the more highly conducting samples, it was found essential to crush the pellets to prevent the well-known electromagnetic "skin effect"

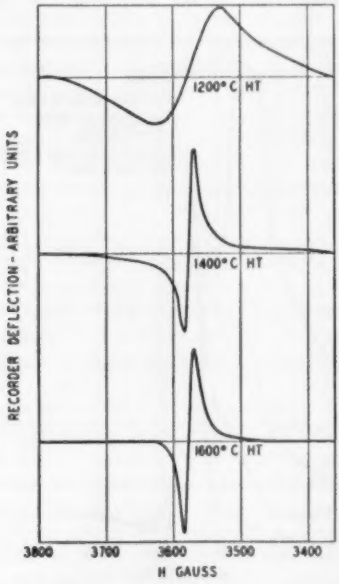

FIG. 2.—Typical line shapes in heat treated channel black.

from shielding the interiors from the microwave field. A light crushing between sheets of paper was found to be equally as effective as grinding with mortar and pestle; hence, all measurements were made with lightly crushed samples. The criterion used for establishing the absence of "skin effect" was invariance of signal intensity upon further grinding. Samples of Spheron 6 from each heat treatment were prepared for electron spin resonance examination in four ways: in air, immersed in benzene, evacuated for 26 hr to 0.01 μ at room temperature, and evacuated for 26 hr to 0.01 μ at 260° C with several helium flushes. These represent successive attempts to remove adsorbed molecular oxygen.

Commercial carbon black samples were prepared similarly. The samples used and their sources are listed below.

Philblack A	Phillips Chemical Company
Philblack O	Phillips Chemical Company
Philblack I	Phillips Chemical Company
Philblack E	Phillips Chemical Company
Wyex	J. M. Huber Corporation
Acetylene Black	Shawinigan Chemicals, Ltd.
P-33	Thermatomic Carbon Company
Lampblack 888	R. W. Greeff and Company
Spheron 6	Godfrey L. Cabot, Inc.

RESULTS

HEAT TREATED CHANNEL BLACK

The width of the electron spin resonance line is illustrated in Figure 1. The line width below 1200° C HT is very sensitive to the presence of air. No attempt was made to connect the high- and low-temperature curves, since they appear to have separate origins. Figure 2 illustrates the nature of this linewidth transition. The wide line of 1200° C HT continues, somewhat broader and weaker, at 1400° C, but a new narrow line is also evident. The broad-line component of the 1400° C HT sample is readily discernible, but its width cannot be measured accurately because of interference from the narrow line. Gain settings are not comparable for the curves in Figure 2, and the intensity of the 1400° C HT curve is weakest of the three. The "cavity resonance" tilted baseline has been removed in these (replotted) spectra. The line widths for the well-evacuated series are compared at 25° C and −189° C in Table I.

TABLE I

ELECTRON SPIN RESONANCE LINE WIDTH OF DEGASSED[a] HEAT TREATED SPHERON 6 CARBON BLACK

Heat treatment	Line width in gauss	
	At 25° C	At −189° C
Original (250)	1.5	0.72
500	1.3	0.87
750	3.4	1.9
1000	6.4	5.6
1200	51	43
1400	3.1	3.1
1600	2.8	2.1
2000	5.7	5.1
3000	2.7	2.4

[a] Degassed at 250° C for 26 hr. with several helium flushes, to less than 0.01 μ Hg.

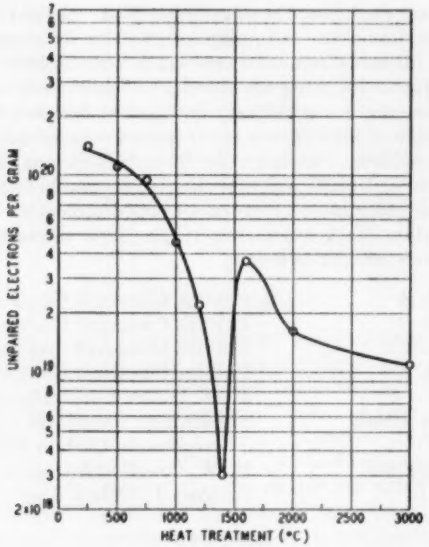

FIG. 3.—Unpaired electron concentration in heat treated channel black (degassed at 250° C).

The spin concentrations are shown in Figure 3. Total spin concentration is shown at 1400° C HT since it was not possible to separate the two lines uniquely. The spin species present below 1400° C appears quite distinct from that present above 1400° C; the low-temperature variety evidently disappears just as the high-temperature species is being formed. The *g* factors are shown in Figure 4 for the samples in air, in benzene, and after degassing at 250° C with several helium flushes.

COMMERCIAL CARBON BLACKS

The commercial carbon blacks differ considerably in line width and in the effect of air upon line width. On the other hand, roughly comparable spin concentrations and *g* values are found. The data are listed in Table II. In both the heat-treated series and the commercial carbon blacks, the base-line correction is much more difficult when the lines are wide. Assays on wide lines are apt to be rather low; consequently, only assays for the well-evacuated samples have been included.

DISCUSSION

HEAT TREATED CHANNEL BLACK

It appears that the unpaired electrons present in channel carbon blacks and in such material heat treated to 1400° C are somewhat similar to those existing in low-temperature, amorphous chars (below 1000° C). The characteristics shared by the unpaired electrons in carbon black and the low-temperature chars include line-broadening when exposed to oxygen[7,12–16], line-broadening with increasing heat treatment[12–16], disapperance of the line when heat treated in the range 1000 to 1400° C[3,4,15,17,18], and a general decline of the *g* value with increasing heat treatment[13]. The electron spin resonance observed in channel

black heat treated in the range 1400 to 3000° C bears a certain similarity to that reported for graphitized chars and very pure graphite[2,19], in that the line width is relatively narrow, the line width is little affected by oxygen, and the g value rises with increasing heat treatment. The resonance differs from that reported by Hennig and Smaller[20], who reported that the integrated absorption (spin assay) fell at lower temperatures of measurement. Tentative results for both the 750 and 1600° C HT samples at liquid nitrogen temperature are consistent with a constant assay and a normal Boltzmann rise of intensity.

The similarity of the resonance in carbon blacks and low-temperature chars is remarkable when one considers the enormous differences in structure of the two types of materials. The former contain well-defined, even though turbostratic, quasi-graphitic crystallites; the latter are amorphous. Heat treatment of the low-temperature chars to the point of incipient crystallinity destroys their original spin content. Extensive recrystallization re-establishes a resonance[2], but this is clearly related to the "new" resonance which appears in carbon blacks at 1400° C since it survives with little change to 3000° C. Another difference between chars and carbon blacks is in their electrical conductivity. For example, at the point of maximum concentration of "low-temperature" spins the specfic resistivity of carbon blacks is less than one ohm cm[6]; it is about 10^{15} ohm cm for an amorphous char prepared from polydivinyl benzene[6]. It is interesting to note that the low-temperature spins in Spheron 6 channel black are capable of surviving higher heat treatment temperatures than those found in chars (1400° vs. 700 to 1000° C).

The spin assay indicates that 1.4×10^{20} unpaired electrons per gram are initially present. The number of quasi-graphitic molecules per gram is readily calculated from the layer diameter[21] of 26 A, the layer spacing[21] of 3.54 A, and the helium displacement density[21] of 1.93 to be 3.2×10^{20}. The actual number of such molecules is probably somewhat larger in that the desired average is the number average and the x-ray method gives an average closer to the weight average. It is evident that there was always fewer than one unpaired electron per quasi-graphitic molecule.

The extreme sensitivity of the line width to molecular oxygen below 1000° C HT, and the fact that there is no separation of the line into broad and narrow components, suggest that most of the spins are accessible to adsorbed oxygen.

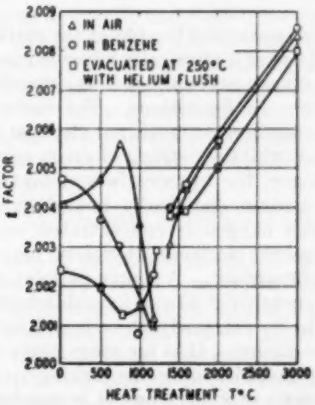

FIG. 4.—g value of heat treated channel black.

TABLE II

ELECTRON SPIN RESONANCE DATA ON COMMERCIAL CARBON BLACKS

Sample	Preparation	10^{-19} × No. spins/g	ΔH (gauss)	g factor
Philblack A	*A*[a]		28	2.0035
	B[b]		16	2.0006
	C[c]		15	
	D[d]	10	15	
Philblack O	*A*		54	2.0031
	B		46	2.0043
	C		41	
	D	8.0	29	
Philblack I	*A*		92	2.000
	B		78	2.001
	C		60	
	D	9.2	41	
Philblack E	*A*		133	1.998
	B		94	2.001
	C[e]		46	
	D	8.1	20	
Wyex	*A*		14	2.0023
	B		3.7	2.0026
	C		2.8	
	D	15	1.1	
Acetylene Black	*A*		4.8	2.0031
	B		3.8	2.0034
	C		3.7	
	D	3.8	3.3	
Thermal (P-33)	*A*		18	2.0019
	B		13	2.0033
	C		13	
	D	5.9	12	
Lampblack 888	*C*		4.2	
	D	5.8	4.1	
Spheron 6	*A*		31	2.0041
	B		11	2.0047
	C		5.3	
	D	13.9	1.5	2.0024

[a] *A*—crushed, in air.
[b] *B*—crushed, in benzene.
[c] *C*—crushed, in vacuum of 0.01 μ
[d] *D*—crushed, evacuated to 0.01 μ at 250° C, with several helium flushes.
[e] Sample was inadvertently helium flushed during evacuation.

This indicates that the spins are either located at the surface or possess sufficient mobility to pass repeatedly near a physically adsorbed oxygen molecule. Now it is likely that combined oxygen plays a part in the stabilization of the unpaired electrons through resonance configurations. For instance, Akamatu et al.[22] have shown that oxygen stabilizes an unpaired electron in violanthrone to the extent that this compound exhibits a strong electron spin resonance spectrum, while its unoxidized analogue, the hydrocarbon violanthrene, does not. Carbon blacks, in general, contain chemically bound oxygen and independent evidence suggests that this oxygen is concentrated mainly in the surface[23]. A large portion of the unpaired electrons, therefore, may be expected to reside in crystallites exposed to the surface. A simple calculation shows that for some of the blacks of this study, notably P-33 and Lampblack 888, the surface packing of the spins would have to be extremely close (ca. 4 to 5 A) if all spins were stictly localized at surface atoms. It is far more likely that the spins possess mobility within each quasi-graphitic molecule making up the crystallite. Since such mobility is characteristic of π electrons, it is concluded that the unpaired spins in the carbon blacks under consideration (up to 1400° C HT) are most

likely π electrons. Above 1400° C HT, very little oxygen sensitivity is found and this suggests immobile unpaired electrons distributed through the bulk phase.

It is considered unlikely that these spins are directly related to conduction holes or electrons. It is unfortunate that sufficient evidence is not at hand to determine the carrier concentration as a function of heat treatment. However, the maximum of conductivity[8] occurs at 1400° C HT where the spin assay is a minimum, and this suggests that an identification of the unpaired spins with current carriers would be difficult. Moreover, the work of Pinnick[24] suggests that no great change in number of current carriers takes place in soft carbons heat treated in the range of 800 to 2000° C.

The presence of molecular oxygen severely broadens the line in channel black and its derivatives up to 1000° C HT. Singer et al.[13] have shown that this results from a shortening of spin-lattice relaxation time in low-temperature chars prepared from sucrose. This could not be verified for the present series because of insufficient microwave power to achieve saturation throughout the series. This broadening decreases the accuracy of the assay greatly since, for example, a tenfold increase in line width results in a hundred-fold decrease in signal amplitude. The assay is likely to be too low because of the tendency to stop the numerical integration procedure when the signal disappears in the noise level. There are also the practical difficulties of correcting for cavity-resonance base-line and of maintaining linearity of sweep over the wider scans needed. It has been reported that oxygen reversibly "eradicates" unpaired electrons in charred materials[5,25]. It is felt to be more plausible, at least for carbon blacks, to conclude that an apparent reduction of the spin assay results from experimental difficulties when oxygen is present

A complete analysis of the facts influencing the line width of this series of heat treated channel blacks is not possible with the information at hand, but a start in this direction is possible. The experiments of Singer et al.[13] on sucrose chars indicates that the line width below 600° C HT is controlled by spin-spin relaxation effects, and suggest that $T_1 = T_2$ above this temperature. In the present work, the klystron power output was not sufficient to adequately saturate the full series of heat treated channel blacks, but it was noticed that the first few members of the heat treatment series saturated more readily than the remainder. Singer[13] showed that the sucrose chars saturated more easily than α,α-diphenyl-β-picryl hydrazyl, and that the ease of saturation decreased with heat treatment. All the carbon blacks examined saturated with more difficulty (greater microwave power) than did α,α-diphenyl-β-picryl hydrazyl.

There is some evidence that the narrow lines observed in the channel blacks heat treated at up to 750° C are exchange narrowed. The minimum line width expected from electron dipole-dipole broadening may be estimated[26] by assuming a Gaussian line shape, a cubic lattice of spins, and a concentration of spins of n per gram,

$$\Delta H = g\beta n\rho[5.1\ S(S+1)]^{\frac{1}{2}}$$

where ΔH is the line width in gauss, g is about 2, β is the Bohr magneton, S is the electron spin of one-half, ρ is the density (assumed to be 1.8 for carbon black), and 5.1 is the numerical value of several pooled physical constants. This leads to line width estimates of 9, 7, and 6 gauss for the original (250° C degassed), 500°, and 750° C HT samples, and these exceed considerably the measured line widths of 1.5, 1.3, and 3.4 gauss, respectively. Hence some narrowing mechanism is present, most likely exchange narrowing since molecular motion is not feasible in these solids.

The rapid increase in line width above 1000° C HT is difficult to understand. The spin assay decreases in this region. Electron dipole-dipole broadening is possible if the electrons are heterogeneously distributed but are prevented, perhaps structurally, from exchange-narrowing the line. Spin-lattice time reduction from near collisions with current carriers has been suggested by Uebersfeld.[14] A third possibility is that the breadth of the line results from an unresolved distribution of lines of different g values. A choice between these alternatives does not seem possible at present.

In the region of 1400 to 3000° C HT, the concentration of unpaired electrons is somewhat less than that present initially. Hence it is unnecessary to invoke a narrowing mechanism to explain the moderately narrow lines which result. It is useful to inquire into the nature of the unpaired electrons present. Ubbelohde[26] has suggested that an electron spin resonance should be expected from certain defect structures in a partially graphitic lattice becuase of free carbon valencies, and has given an example of such a defect which he calls a "claw" dislocation. There is room for one, but not two, protons at the edge of the open hexagon at a hole in the lattice if planarity is retained. This results in just the immobile σ type of unpaired electron postulated here. We have some evidence that defect structures are in fact the origin of the spin species observed in this series, in that the unpaired spin concentration is a maximum at 1600° C HT. The most rapid increase in layer dimension[8] occurs at this temperature and it is reasonable to expect a maximum in the defect content at this same content through annealing and a decrease of unpaired spins is observed at 2000 and 3000° C HT.

A good part of the line width in the 1400 to 3000° C HT series may be explained by proton-electron broadening according to the model of the "claw" defect. The near proton produces at the σ-electron position a magnetic field of about ± 4 gauss, and the actual line width depends upon a suitable averaging of this plus other proton contributions. Dispersion of the g values may also contribute to the line width to a lesser extent. It is hoped that the use of a deuterated feedstock will settle this point.

COMMERCIAL CARBON BLACKS

The unpaired spins present in the commercial carbon blacks listed in Table II can probably be ascribed to unpaired π electrons, although acetylene black may be an exception. The latter has a rather large diamagnetic susceptibility suggesting highly graphitic character, and hence may resemble graphitized blacks in other respects also. It is not the intent of this paper to correlate the nature of the unpaired spins with the many variables which distinguish these carbon blacks. It is, however, interesting to note that an increasing temperature of formation, e.g., from channel to furnace blacks, results in broadened lines and less oxygen sensitivity similar to that found for the channel black series. The unpaired electron concentration differs among these commercial blacks by only a factor of four, although the surface areas differ by a factor of twenty.

ORIGIN OF UNPAIRED ELECTRONS IN CHARRED MATERIALS AND CARBON BLACKS

It appears possible to give at least a plausible explanation of the occurrence of unpaired electrons in charred organic material. The formation of condensed aromatic rings is one of the initial effects of charring. With further heat treat-

ment these aggregates gain in size and, particularly when attached to an electronegative group such as quinone-type oxygen (known to exist in carbon black), become capable of stabilizing an unpaired π electron via resonance configurations. Unpaired electrons are copiously produced by the accompanying devolatization. The number which survive depends upon the number of molecules of sufficient size and composition to stabilize them.

With increasing heat treatment, the number of independent molecules of sufficient size for stabilization continues to grow until merging of these molecules into larger units occurs. With each combination of two independent molecules, two stabilizing sites become one and the concentration of unpaired electrons decreases. Toward 1400° C, the postulated combination of stabilizing units is esssentially complete and few unpaired π electrons survive. Porosity, of course, allows oxygen to penetrate near such trapped electrons, but the mobility characteristic of π electrons is essential to effective broadening via reduction of spin-lattice relaxation time.

It appears that the unpaired spins of carbon black depend rather heavily on oxygen-containing groups for stabilization. Let us suppose that the quasi-graphitic layer molecules are the stabilizing sites for the unpaired π electrons. It has already been shown that the number of unpaired electrons in each "molecule" does not appear to exceed unity at any of the spin concentrations observed. During the early stages of heat treatment (up to 1200° C) considerable devolatilization occurs with loss of CO, CO_2 and hydrogen[8]. The number of bonds broken exceeds greatly the number of stabilizing sites left, but most of the broken bonds will recombine without leading to a stable unpaired electron. At the same time the layer diameter, L_a, increases only very slightly and the height of the crystallite L_c does not change at all.[8] Between 1000 and 1400° C, L_a increases appreciably and this leads to a decrease in the number of stabilizing sites. However, L_a only doubles at the most, while the spin concentration drops a hundredfold. The large drop could be explained by postulating some sort of a cross-linking mechanism capable of combining the stabilizing sites without leading to extensive layer growth detectable by x-ray diffraction or destroying the chemical resonance in the bond system. This does not appear too likely. It seems more plausible that the removal of oxygen sites from the surface deprives the carbon black "molecules" of their ability to stabilize the unpaired spins[22]. The removal of combined oxygen begins near 250° C and continues up to 1200° C[8], where over 80% of the spins have disappeared. It thus covers the range in which crystallite layer growth cannot account for a reduction in stabilizing sites.

The appearance of the new spin species at 1400° C offers no difficulty. The first significant increase in L_c occurs at this temperature and the maximum rate of growth in L_a occurs between 1400 and 2000° C[8]. This is clear evidence of recrystallization. The wholesale reshuffiing of the condensed rings would be expected to produce a great many lattice defects at which σ electrons are trapped, perhaps as in the claw dislocation[27] or similar structures.

CONCLUSIONS

Two types of unpaired electrons have been observed in a heat treated channel process carbon black. In the original black, and for this material heat treated up to 1400° C, the unpaired electrons are believed to consist of unpaired mobile π electrons stabilized by resonance energy in large condensed ring structures, many of which probably contain oxygen. These disappear with heat treatment

above 1400° C and a new species of unpaired spins appear which have been assigned to localized σ electrons at defects in the graphitizing lattice. The unpaired electrons in most commercial carbon blacks are believed to be π electrons, similar in concentration and g value, but varying considerably in line width and oxygen sensitivity. The highly graphitic acetylene black may contain σ electrons also, for its line width is little affected by oxygen. A tentative explanation has been formulated for the origin of unpaired electrons in charred materials and carbon blacks.

SYNOPSIS

An appreciable concentration of unpaired electrons has been found in colloidal carbon blacks through the application of electron spin resonance spectroscopy. The unpaired electrons in a typical channel process carbon black, Spheron 6, have been studied by noting the changes in the electron spin resonance spectrum produced by heat treatment (HT) to 3000° C and by various degrees of evacuation of the sample. The results indicate that the unpaired electrons in the original material are mobile π electrons, which are stabilized by condensed aromatic ring structures. Their concentration decreases slowly to 750° C HT and then declines more rapidly and vanishes above 1400° C HT. A different species of unpaired electrons arises at 1400° C HT. These are believed to be immobile σ electrons resulting from broken carbon-carbon bonds at lattice defects. The unpaired electrons present in several commercial carbon blacks have been examined and are believed to be π electrons also. A tentative theory of the origin of the unpaired electrons is given.

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ELECTRON PARAMAGNETIC RESONANCE INVESTIGATION OF VULCANIZATION *

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New and extensive prospects are being developed with the employment of electron paramagnetic resonance[1] (radiospectroscopy) (EPR) for the investigation of the chemical reactions taking place in the vulcanization of rubber. It is well-known that molecules which are taking part in chemical reactions in the majority of cases pass through the state of forming chemically active free radicals in which there are electrons having unpaired spins, i.e., the radicals have magnetic moments. Observation of the occurrence and disappearance of free radicals in chemical processes may be effected by the investigation of the paramagnetic resonance absorption of these radicals. Measurement of the radiofrequency of any given compound makes it possible to determine the degree of dissociation into free radicals. Consequently it becomes exceptionally valu-

Table I

Composition of the stock	No. of specimen							
	1	2	3	4	5	6	7	8
Natural rubber	100	100	100	100	—	—	—	—
Polyisobutylene	—	—	—	—	100	100	100	100
TMTD	3.0	3.0	3.0	—	3.0	3.0	3.0	—
Zinc oxide	—	5.0	5.0	—	—	5.0	5.0	
Stearic acid	—	—	2.0	—	—	—	2.0	
Sulfur	—	—	—	3.0	—	—	—	3.0

able to employ EPR to solve the question of the nature of the reactions which take place in vulcanization. If in point of fact vulcanization is a radical reaction, then we ought to be able to observe EPR spectra.

All our investigations[2, 3] were carried out with a radiospectrometer, developed in the laboratory of S. E. Bresler, which possesses high sensitivity (e.g., for $2 \cdot 10^{-2}$ mole of diphenyl picryl hydrazyl, by means of which the sensitivity of the apparatus is generally calibrated). We investigated the vulcanization of natural rubber by tetramethylthiuram disulfide (TMTD) in the presence of zinc oxide and stearic acid. In parallel with this we investigated analogous stocks in which the natural rubber was replaced by polyisobutylene. Thus we were looking at two systems differing from each other in the presence or absence in the polymer structure of double bonds. The composition of the stocks for which the EPR spectra were studied is given in Table I.

The unvulcanized stocks were placed in ampoules of a high-quality quartz which contained no paramagnetic admixtures of any kind; after partial evacuation of air the ampoules were sealed. Then the ampoules were placed in the resonator, which was heated from 20° to 220° according to a set program.

* Translated by R. J. Moseley from *Doklady Akad. Nauk SSSR* **129**, No. 2, 361–4 (1959); RABRM translation 790.

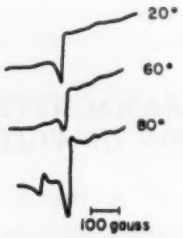


FIG. 1.—Formation of polar radicals on heating of natural rubber with 3% tetramethylthiuram disulfide (TMTD) at 20 to 80°.

Parallel to these experiments we observed the EPR spectra of a rubber subjected to 30 min mastication on the mill, without additions of any kind. It was established that the original rubber (pale crepe) when not subjected to mastication did not exhibit paramagnetic spectra. The rubber subjected to mastication was characterized by the presence of one spectral line, which indicates, apparently, the formation of peroxide radicals as a result of oxidative processes (Figure 1).

Furthermore this spectrum line is observed in a compound of rubber with TMTD and other ingredients before heating, i.e., before vulcanization. As the temperature was raised vulcanization by TMTD led almost to an instantaneous (i.e., in less than a minute) increase in the complexity of the paramagnetic spectra. At 60° we observe deformation of the spectrum line, at 80° there occur two, at 120° three, and at 140 to 160° four paramagnetic spectrum[2, 3] lines. With further heating at increased temperatures (180, 200, 220°) we observe in the course of the first 10 to 20 min at 220° an increase in the intensity of the paramagnetic spectra with their subsequent extinction. After 20 min at 200°, or after 5 to 7 min at 220° from the beginning of heating, there takes place a converse alteration in the paramagnetic spectra, in which the four lines gradually become three (a simple triplet as an intermediate stage), which then, after cooling, gradually disappear and there remains the original isolated peak (Figures 2 and 3).

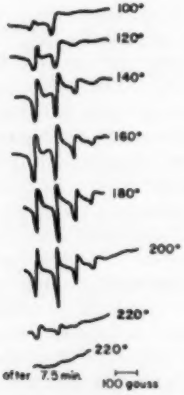


FIG. 2.—Kinetics of formation of polymeric radicals in the vulcanization of natural rubber with 3% TMTD at 100 to 200°.

In our experiments it was established that the zinc oxide and stearic acid present in the stock did not exhibit any significant influence upon the character of the paramagnetic spectra. Renewed heating of the stocks (the vulcanizates) led to the formation of paramagnetic spectra of almost the same intensity. Thus the EPR which was observed in the case of heating natural rubber (pale crepe) in the presence of TMTD, zinc oxide and stearic acid is a convincing demonstration of the radical character of the vulcanization reactions. On the other hand, experiments in heating stocks of analogous composition, but with the replacement of natural rubber by polyisobutylene, demonstrated that no paramagnetic spectra of any kind were to be observed at any of the temperatures under investigation. From this example we get a good illustration of the

FIG. 3.—Kinetics of formation of polymeric radicals in the vulcanization of natural rubber with 3% TMTD at 200°: *1*—after 5 min, *2*—10 min, *3*—16 min, *4*—22 min, *5*—27 min, *6*—32 min, *7*—after cooling for an additional day.

part played by the double bonds of the polymer; their absence from polyisobutylene resulted in there being no vulcanization, and in addition paramagnetic spectra were absent.

Vulcanization of natural rubber by sulfur (without TMTD) likewise did not give paramegnatic resonance spectra. The obtaining of paramagnetic spectra allows us to conclude that in the vulcanization of natural rubber by mean of TMTD polymeric radicals are formed, since any low-molecular weight radicals —products of dissociation of TMTD—would easily recombine at vulcanization temperatures of 140 to 200°, when the coefficient of diffusion is certainly high. At the temperatures under investigation the life of the polymeric radicals is evidently sufficiently long. Repeated heating leads to the formation of new chains of polymeric radicals which recombine on continued heating to form three-dimensional structures. An orientative calculation shows that in our experiments in vulcanization of rubber the concentration of the polymeric

radicals was $4 \cdot 10^{-7}$mole/g. The spectra observed are undoubtedly complex, and their individual parts appear and disappear at different times. Further investigations on model systems employing labelled isotopes of the various elements of the structure of TMTD and of the polymer may lead to the proper interpretation of such spectra. On the basis of the existing experimental data from various investigators[4, 5, 6], the process of dissociation of TMTD into radicals, the formation of polymeric radicals and their recombination with the formation of three-dimensional structures (vulcanizates) may be presented as follows:

1) Dissociation of TMTD into radicals:

a) $(CH_3)_2N-\overset{\overset{S}{\|}}{C}-S-S-\overset{\overset{S}{\|}}{C}-N(CH_3)_2 \rightleftharpoons 2\left[(CH_3)_2N-\overset{\overset{S}{\|}}{C}\cdot\right] + \cdot S-S\cdot$

b) $(CH_3)_2N-\overset{\overset{S}{\|}}{C}-S-S-\overset{\overset{S}{\|}}{C}-N(CH_3)_2 \rightleftharpoons 2\left[(CH_3)_2N-\overset{\overset{S}{\|}}{C}-S\cdot\right]$

c) $(CH_3)_2N-\overset{\overset{S}{\|}}{C}-S-S-\overset{\overset{S}{\|}}{C}-N(CH_3)_2 \rightleftharpoons (CH_3)_2N-\overset{\overset{S}{\|}}{C}\cdot + \cdot S-S-\overset{\overset{S}{\|}}{C}N(CH_3)_2$

2) Formation of polymer radicals:

$$(CH_3)_2N-\overset{\overset{S}{\|}}{C}-S\cdot + \sim CH_2-\overset{\overset{CH_3}{|}}{C}=CH-CH_2\sim \xrightarrow{t}$$

$$(CH_3)_2N-\overset{\overset{S}{\|}}{C}SH + \sim CH_2-\overset{\overset{CH_3}{|}}{C}=CH-CH\sim \quad \sim CH_2-\overset{\overset{CH_3}{|}}{\dot{C}}-CH=CH\sim$$

3) Recombination of the polymer radicals, formation of three-dimensional structures, with incorporation of TMTD radicals into the structure of the rubber:

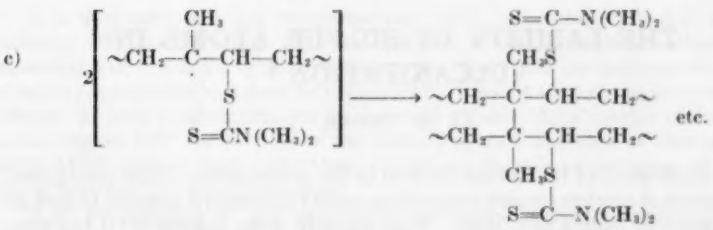
a) $\sim CH_2-\overset{\overset{CH_3}{|}}{C}=CH-\dot{C}H\sim + \sim CH_2-\overset{\overset{CH_3}{|}}{\dot{C}}-CH=CH\sim \longrightarrow$

$$CH_2-\overset{\overset{CH_3}{|}}{C}-CH=CH\sim \quad \sim CH-CH=\overset{\overset{CH_3}{|}}{C}-CH_2\sim$$

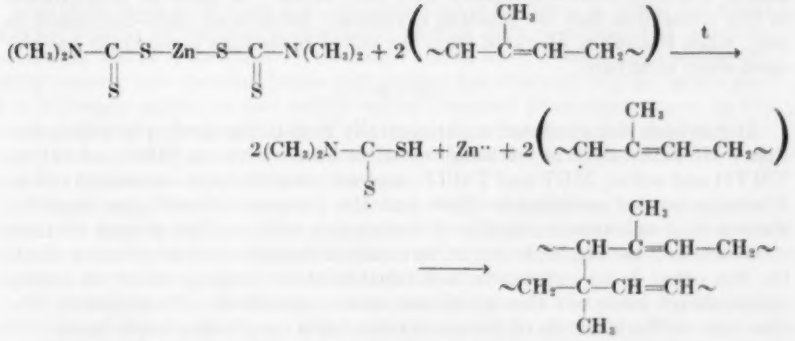
b) $\sim CH_2-\overset{\overset{CH_3}{|}}{C}=CH-CH_2\sim + S-\overset{\overset{S}{\|}}{C}-N(CH_3)_2 \longrightarrow \sim CH_2-\overset{\overset{CH_3}{|}}{\dot{C}}-CH-CH_2\sim$

$$\overset{\overset{S}{|}}{S=C}-N(CH_3)_2$$

c)



The possibility is not ruled out that the zinc dimethyldithiocarbamate formed during vulcanization facilitates the transformation of the rubber into a three-dimensional structure, by accepting hydrogen from the α-methylene groups of the rubber.



Our experiments on the vulcanization of rubber with sulfur in the presence of DPG at temperatures of 100 to 160° did not reveal the formation of paramagnetic spectra, which fact indicates essential differences in the mechanism of vulcanization of rubber by TMTD and sulfur in the presence of a vulcanization accelerator. Thus the EPR spectra observed in the vulcanization of natural rubber by TMTD serve as an experimental demonstration of the radical character of the reactions taking place in this process.

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THE LABILITY OF SULFUR ATOMS IN VULCANIZATION *

G. A. Blokh

The application of the isotope method to the investigation of the mechanism of the action of accelerator and vulcanizing agents has made it possible to look at this question in quite a new light. With the help of the isotope S^{35} it has been demonstrated that in the process of curing there takes place a continuous exchange of atoms of sulfur in the structure of the accelerators, and of elementary sulfur as a vulcanizing agent, with the formation of unstable intermediate compounds. The sulfur thus liberated undoubtedly has high energy, as a result of which it combines rapidly with the rubber. It must be remembered in this connection that the reacting elementary sulfur is an eight-membered S_8 ring, while the sulfur liberated from the sulfur containing compounds has the open chain structure:

$$\cdots\!-\!S\!-\!S\!-\!\cdots.$$

It has been demonstrated experimentally that in the process of vulcanization there takes place an exchange of sulfur atoms between MBT and sulfur, TMTD and sulfur, MBT and TMTD, and sulfenamide accelerators and sulfur. A comparison of accelerator effect and the presence of exchange reactions showed that substances capable of exchanging sulfur which is part of their structure, i.e., having labile sulfur, have also a characteristic accelerator effect. On the other hand substances not capable of exchanging sulfur at curing temperatures have not this additional accelerator effect. Consequently the structure of the molecule of the accelerator takes on primary importance.

It must be noted in particular that in the process of vulcanization as a chain reaction there take place a series of continuous complex chemical reactions. During this process there are formed new sulfur-containing compounds (H_2S, ZnS, zinc salts of accelerators and so on) which also do not remain in the nonlabile state and which take part in exchange reactions. It is known that during vulcanization there takes place the formation of zinc mercaptides, which on decomposing form disulfide or monosulfide bridges between the chains of rubber liberating at the same time zinc sulfide:

$$R\cdot S\cdot Zn\cdot S\cdot R_1 + S \longrightarrow \begin{cases} R\!-\!S\!-\!S\!-\!R_1 \\ \\ R\!-\!S\!-\!R_1 \end{cases} + ZnS$$

On the interaction of the sulfur with the rubber and the other components there is formed hydrogen sulfide, which decomposes into radicals:

$$H_2S \rightleftharpoons H^{\cdot} + HS^{\cdot}$$

and takes part in the formation of sulfur structures in the rubber.

In our investigations it was demonstrated experimentally that the zinc sulfide actively exchanges atoms of sulfur with elementary sulfur. After melting radioactive zinc sulfide with ordinary, nonactive sulfur for 60 min at 145° the sulfur separated from the melt acquired radioactivity of up to 300 to 400 imp/min and more.

* Translated by R. H. Moseley from *Legkaya Prom.* 14, No. 1, 45-7 (1954); RABRM translation 787.

It is demonstrated that on contacting MBT and radioactive zinc sulfide (activity 3000 to 4000 imp/min) for 120 min at 145° the MBT which was separated had low activity (62 imp/min), i.e., there was no exchange of atoms of sulfur; apparently this may be explained by the fact that at the temperature referred to both components are in the solid phase. As a matter of fact the contacting at 145° for 60 min of the ternary system radioactive zinc sulfide-sulfur-MBT showed that under these conditions there is an exchange of sulfur atoms between all the components.

It is established that hydrogen sulfide liberated during vulcanization also takes part in exchange reactions with sulfur-containing components. We prepared radioactive hydrogen sulfide H_2S^{35}, and with it treated MBT at 100° and 145° for varying times.

After separation the MBT acquired radioactivity. The exchange of atoms of sulfur reached 70%.

All these facts go to show that vulcanization is a process in which the sulfur is in continuous movement: it enters into various sulfur-containing compounds, extracting sulfur from them in the more active open chains. Consequently, sulfur coming into chemical bonds with rubber has different origins: in one case it is hydrogen sulfide or zinc sulfide sulfur liberated from accelerators, in the other during the decomposition of the polysulfide bonds in the rubber or directly from elementary sulfur in the decomposition of the eight-membered ring and the formation of active sulfur radicals.

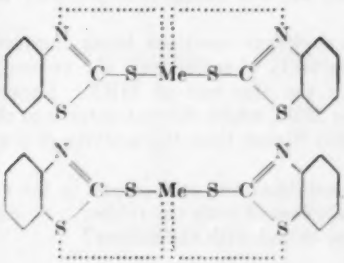
Thus the structural changes in rubber during vulcanization are the result of numerous continuous exchange reactions between sulfur-containing components, as a result of which sulfur is liberated in the active form of open chains and converts the rubber into a three-dimensional structure.

As is well-known, zinc oxide in vulcanization plays an important part as an activator of the accelerators. We consider it important to establish the influence of zinc oxide upon the course of exchange reactions between accelerator-vulcanizing agents. In this connection we studied exchange reactions between MBT and sulfur in the presence of zinc oxide both in melts and SKB (sodium butadiene) vulcanizates.

It was established that in the presence of zinc oxide the exchange of sulfur atoms is retarded. If the percentage of exchange of atoms of sulfur between the thiol sulfur of the MBT and the free sulfur in the rubber at the time of vulcanization at 145° for 15 min is 14% in the absence of, in the presence of zinc oxide it goes down to 6%.

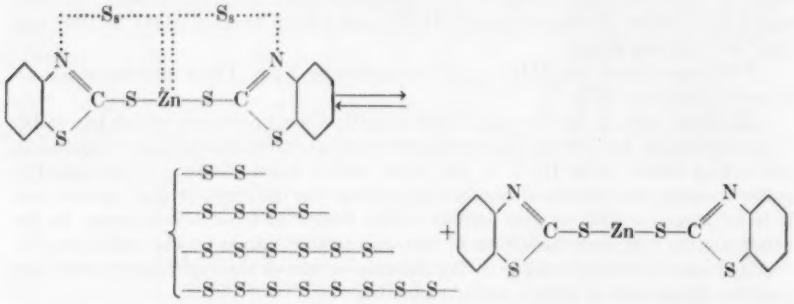
How are we to explain the activating properties of zinc oxide and its retarding influence upon the exchange of atoms of sulfur?

As is well-known, in the interaction of MBT with metals of the second group there are formed complex salts of the following structure:

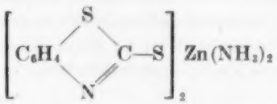


where the metal (Me) is bound by supplementary valencies with the sulfur or nitrogen. It is evident that under these conditions the lability of the sulfur in the zinc salt alters, the conditions for tautomerization disappear and as a result of this the exchange reactions are retarded.

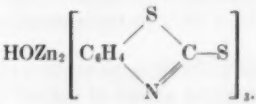
Apparently on account of these supplementary valencies there takes place an addition of the eight-atom ring molecules of sulfur to the zinc salt, with the formation of unstable compounds, capable of easily splitting off sulfur in the form of open active sulfur chains at the temperature of vulcanization (a catalytic process).



In addition it must be taken into account that depending upon the conditions of the medium the zinc salts may have a different structure and consequently a different influence upon the exchange reactions. If the formation of the zinc salt of MBT takes place in an ammonia solution, we get a salt of the following composition:



If on the other hand the salt is produced in alcoholic alkali, it has a different composition:



We must suppose that there are formed in the vulcanized rubber zinc salts of varying structure, which are not identical in the way they take part in the exchange reactions.

In the event of the exchange reactions being completed before the salt is formed, there is the possibility of sulfur from the vulcanization agent entering into the composition of the zinc salt of MBT. Experiments confirm this. The radioactivity of the MBT which did not enter into the composition of the zinc salt was considerably higher than the activity of the MBT from the zinc salt.

It was necessary to establish the part played in the exchange reactions by sulfur which is chemically bound with the rubber.

Is the sulfur labile or bound with the rubber?

To decide this question separate experiments were carried out with vulcanizates in which there was monosulfide sulfur and a collection of polysulfidically bound sulfur.

We prepared vulcanizates of SKB and SKS-30 (butadiene-styrene rubber with 30% styrene) on the basis of TMTD alone (4 parts to 100 parts of rubber). It is well-known that TMTD vulcanization leads to the formation of monosulfide bridge bonds of the —C—S—C— type, which are characterized by a high energy of the bonds, amounting to 45.5 kcal/mol.

The vulcanizate with TMTD was subjected to acetone extraction for 50 hr to remove free sulfur-containing decomposition products of TMTD, which ought not to take part in exchange reactions. After this the vulcanizate was boiled for 24 hr in a xylene solution of radioactive MBT, tagged with sulfur in the thiol group. The activity of the original MBT was 200 imp/5 min. The radioactivity of the extracted MBT did not alter after 24 hr boiling in xylene with the vulcanizate. This is a convincing indication of the nonlability of the monosulfide bound sulfur.

We prepared radiovulcanizates of SKB and SKS-30 in the presence of S^{35} alone without sulfur-containing accelerators, but in the presence of DPG. In this case we got vulcanizates in which there were various polysulfide bonds of the —C—(S)—C— type, the energy of whose bonds was 27.5 kcal/mol.

As was shown by Dogadkin and Tarasova, under thermal action the polysulfide bonds are destroyed with the liberation of free sulfur. According to the data of these authors, up to 20% of the total amount of bound sulfur may be extracted during boiling of the vulcanizates in a 10% solution of sodium sulfite. The resulting radiovulcanizates were subjected after 100 hr acetone extraction to boiling in alcohol and xylene solutions of various accelerators. In addition the accelerators were extracted and tested for radioactivity. The data are presented in Table I.

As may be seen from the data, exchange of sulfur atoms does take place. The existence of this exchange is explained by the fact that some of the polysulfide bonds are destroyed during boiling, with the liberation of free sulfur, which also takes part in the exchange.

Radiovulcanizates subjected after acetone extraction to boiling in a 10% solution of sodium sulfite (as a result of which the polysulfide sulfur was removed) did not take part in the exchange reactions. Thus with an activity of the original sulfur of 4000 imp/mg min the activity of the sulfur in the MBT after 10 hr boiling of the radiovulcanizate in a xylene solution of MBT was 25 imp/mg min at the most.

The experimental data presented are evidence that the sulfur monosulfidically bound with the rubber does not take part in the process of exchange of

TABLE I

Accelerator interacting with the sulfur of the vulcanizate	Temperature, °C	Time of heating, hr	Exchange of atoms of sulfur, %
MBT	78	50	0.2
	78	78	5.9
	138	10	6.0
	138	27	3.4
TMTD	120	10	3.0
	120	31	6.0
Sulfenamide	78	80	8.0
	138	28	6.6

sulfur atoms. In the exchange reactions there takes part free sulfur which is continuously liberated by the sulfide bonds in the rubber which are being destroyed. Undoubtedly, after exchange it once again enters into the structure of the rubber.

All the above is evidence that the quality of the resulting vulcanizates depends unconditionally upon the intensity of the exchange reactions which take place during vulcanization, the transfer of the sulfur into the state of active sulfur radicals and the formation of strong structures in the rubber.

Thus the isotope method convincingly demonstrates that the vulcanization of rubber is a continuous chain of interrelated and interpenetrating exchange reactions of atoms of sulfur, which moreover govern the technical effect of vulcanization. There is no doubt that other atoms and components in the complex system of a vulcanization stock also take part in this movement. Of particular significance for the quality of the vulcanizates is the diffusion of the sulfur in the vulcanizing stock. We have demonstrated by the isotope method that there takes place in vulcanized rubber an intensive diffusion of sulfur, and its transfer from one vulcanizate to another in the case of plying-up. As a result we have the possibility of the phenomena of over-vulcanization at the contact interface of two types of vulcanizate, which has a sharply adverse effect upon the quality of the vulcanizates, particularly when operating under repeated deformations.

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MIGRATION AND DISTRIBUTION OF RADIOACTIVE SULFUR IN COMPOUNDED RUBBER *

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In the production of vulcanized rubber articles it is necessary to take into account the possibility of migration of sulfur from one ply into another. It is well-known that alterations in the concentration of sulfur and accelerators in a stock, taking place as a result of diffusion processes, may lead to alteration in the quality of the rubber. In particular, if in formulating mixes for multiply rubber-fabric articles we take into account the migration processes of the accelerating and vulcanizing agents, it becomes possible to prevent the occurrence of various defects through nonuniform vulcanization. Once again, if the unvulcanized stock is stored in piles, migration means that alterations in the concentration of sulfur and accelerators cannot be ruled out.

Another factor closely connected with the quality of the resulting articles is the uniformity of distribution of the sulfur when added to a compounded stock. Thus the study of migration processes takes on considerable practical importance.

One promising method of investigation of diffusion processes in vulcanized rubber may be the use of tagged atoms. With it we can effectively and rapidly investigate migration processes at different stages of manufacture. The significance of this method for the investigation of the mechanism of the action of accelerator and vulcanization agents has already been pointed out in the literature[1]. We used the tagged atom method in the investigation described below . . . a joint investigation by the rubber department of the Kiev Technological Institute of Light Industry, the Institute of Physical Chemistry of the Academy of Sciences of the Ukrainian SSR, and the "Krasnyi Rezinshchik" and "Ukrkabel" works.

Distribution of sulfur in a compounded stock.—Upon the uniformity of distribution of sulfur in a stock there depends whether the mechanical properties of the vulcanized rubber are up to specification. The following experiment was devised. Radioactive sulfur, 1% by amount, was added to a stock on a laboratory mill with a given nip and number of cut-backs. In addition at various stages of mixing we took three specimens from various parts of the mix. The specimens were tested for radioactivity. From the number of radiation impulses of the specimens recorded it was possible to judge the uniformity of distribution of the sulfur in the raw stock. The results are shown in Table I.

From these figures we may conclude that it is only after the fourth to sixth pass through a close nip that identical radioactivity of the specimens is achieved, i.e. uniform distribution of the sulfur in the different parts of the stock, which

* Translated by R. J. Moseley from *Legkaya Prom.* 15, No. 1, 28–30 (1955); RABRM translation 772.

TABLE I

Conditions of mixing of the radioactive sulfur	Thickness of stock in mm	Number of impulses (3 min)		
		Specimen 1	Specimen 2	Specimen 3
Cut-back				
4 cut-backs		1.690	1.032	860
8 cut-backs	2.0–2.5	1.480	1.740	1.300
16 cut-backs		1.520	1.570	1.420
Passes through a close nip				
After second pass		1.560	1.780	1.530
After third pass	1.0–1.2	1.540	1.460	1.430
After fourth pass		1.470	1.465	1.480
After sixth pass		1.430	1.400	1.445

is one of the main prerequisites for producing rubber with constant physical properties.

Migration of sulfur during the storage of stocks.—The technology of rubber production provides for "resting" of the stocks. Sometimes the raw stocks lie in stacks in the intermediate stages of operations for quite a long time (more than 48 h). There is no doubt that under these conditions migration takes place. This again may be demonstrated by means of tagged atoms.

The following experiments were devised: (a) a raw radioactive stock in the form of a sheet of thickness 1.5 to 2.0 mm was placed on a talc-dusted non-radioactive stock; (b) a raw radioactive stock was dusted with talc and placed upon a fabric, frictioned with a raw nonactive stock. Then after a definite time we took specimens of this stock and the frictioned fabric and tested them for radioactivity. The results are given in Table II.

As we see, even with a comparatively short contact of the raw stock and the fabric (at room temperature) we observe migration of the sulfur, which is shown by the occurrence of radioactivity on the frictioned fabric and stock. It was found by experiments, in addition, that with more prolonged contact of the vulcanized radioactive rubber with a raw stock or unvulcanized rubber the stock, or raw rubber, becomes radioactive, which again is evidence of the migration of free sulfur from the vulcanized rubber into the stock or raw rubber.

Migration of sulfur in the course of vulcanization.—In the manufacture of multiply articles made up of a combination of stocks of differing composition (motor tire casings, cable covers, footwear, artificial leather and so on) it is necessary to take into account the diffusion of the sulfur in the course of vulcanization. We studied the migration of sulfur from a raw, radioactive stock into a scorched vulcanizate during their simultaneous vulcanization, the radioactive stock being insulated from the nonactive by talc, fabric or paper (as in cable technology). At the same time we studied the migration of sulfur out of the radioactive cover into the frictioned fabric (separated from each other by talc or paper). It is necessary to use talc or paper in order to separate the

TABLE II

Duration of contact, h	Radioactivity (number of impulses in 5 min)	
	Cover stock	Frictioned fabric
2	1.460	25
24	1.460	74
72	1.390	128
120	1.309	188

TABLE III

Insulation	Duration of vulcanization, min at 135°	Radioactivity (number of impulses per min) of cover stock	Radioactivity (number of impulses per min) of frictioned fabric
Talc	10	600	200
	15	600	380
Paper	10	600	2
	15	600	3

pliedup nonactive rubber or fabric once the vulcanization process has been completed and to carry out the investigation for radioactivity. In this way we included in the experiments various types of contact of stocks and fabric, met with in the rubber industry.

The data on the migration of sulfur from the radioactive stock into the frictioned fabric (at 135°) are given in Table III.

These data show that sulfur migrates from the cover stock into the frictioned fabric through the talc insulation; but insulation of cigarette paper (thickness 0.03 mm) checks migration.

The results of experiments in which we tested the migration of sulfur from a radioactive stock into vulcanized rubber through fabric, talc and paper insulation in the course of vulcanization, are given in Table IV. After vulcanization we cut from each sheet specimens in the form of small circles of diameter 15 mm, which were then investigated for radioactivity by a counter for beta radiations. In the table we show as a fraction the radioactivity of the contact surface (the numerator) and of the reverse side of the specimen (the denominator) in relation to the original radioactivity: between brackets we indicate the thickness of the specimen in mm.

As may be seen, radioactivity is observed at a depth of 1.0 to 1.5 mm, which convincingly confirms the fact of migration of sulfur from a radioactive stock into vulcanized rubber through a fabric layer and talc. However, a paper layer markedly reduces migration.

Investigation of migration processes at different stages of rubber production makes it possible to draw a number of practical conclusions.

TABLE IV

Migration of sulfur from a raw radioactive stock during vulcanization (142°, 60 min)	Radioactivity in % of activity of original stock: Fabric	Sheets: 1	2	3
Into raw stock through fabric insulation	$\frac{8.1}{7.1}$ (0.40)	$\frac{8.5}{6.3}$ (0.14)	$\frac{4.6}{3.8}$ (0.20)	$\frac{2.6}{1.3}$ (8.35)
Into raw stocks through talc insulation	—	—	—	$\frac{2.9}{2.8}$ (1.02)
Into raw stock through paper insulation	—	$\frac{4.0}{2.4}$ (0.15)	$\frac{1.0}{0.4}$ (0.22)	$\frac{0.3}{0.4}$ (0.56)
Into vulcanized rubber through fabric insulation	$\frac{12.0}{11.0}$ (0.42)	$\frac{9.8}{3.0}$ (0.32)	$\frac{1.4}{0.8}$ (0.45)	$\frac{0.5}{0.2}$ (0.20)

In prolonged storage or long-distance shipment of pliedup stocks, when they are of the same, or, more probably, different composition there takes place a shift in the concentration of sulfur which may later become one of the causes of irregularity in the properties of the vulcanizates. Talc insulation does not check migration of sulfur from one stock to another, while paper insulation practically ensures protection from migration.

For sulfur added on the rolls to be uniformly distributed, it is necessary to pass the stock carefully through a fine nip, to ensure uniform vulcanization.

In the vulcanization of multiply specimens and rubber-fabric articles sulfur penetrates from one ply to another, even if they are separated by a fabric layer. It follows from this that in working out formulas for such articles it is necessary to modify the vulcanization recipe; this is not merely of importance in respect to technique and economics, but also to prevent cracking, ply separation and other defects.

THE VULCANIZATION OF RUBBER UNDER HIGH PRESSURE *

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Bridgeman and Conant[1] first observed the polymerization of isoprene, dimethylbutadiene and other monomers under pressure. According to the studies of Starkweather[2], Tammann and Pape[3], Kobeko, Kuvshinskiĭ and Semyenova[4], polymers of isoprene, butadiene and styrene resulting from high pressure are no different than polymers obtained at ordinary pressure. On the other hand a study by Conant and Tongberg[5] and Conant and Peterson[6] showed that at a pressure of 12,000 kg/cm², in addition to a hundredfold increase in the rate of polymerization of isoprene, the formation of new insoluble polymers is observed. Richardson[7] notes this although he adheres to the opinion that polymer structure is independent of pressure. Works of Carothers and

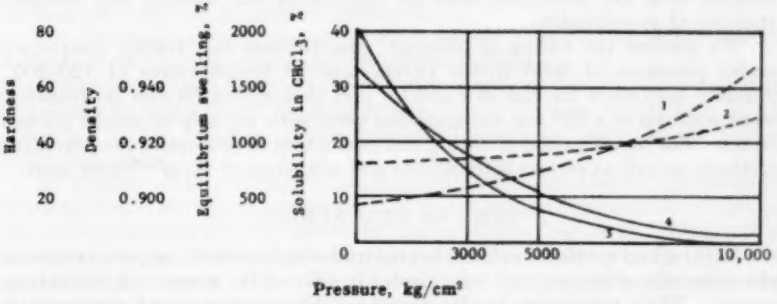

Fig. 1.—Variation of properties of SKB rubber with pressure (temperature 160° for 4.5 hours): *1*—hardness, *2*—density, *3*—swelling, *4*—solubility.

Coffman[8], Veryeshchagin[9], Gonikberg[10], Dintess[11] and others demonstrate the effect of high pressure on the degree of polymerization as well as on the composition and uniformity of the polymer.

Bridgeman[12] first examined the variation of the character of rubber with high pressures in 1923. In more recent works of Bridgeman[13] and also of Scott[14] and Adams and Gibson[15] the physical and mechanical properties of rubber in relation to external pressure are set forth.

The dedicated works of Tiessen and Kirch[16], Dow[17], Wood, Bekkedahl and Gibson[18], Weir[19] and others report the phase transformation of gum rubbers and resins under pressure. Wilkinson and Gehman[20] investigated the vulcanization of rubber under high pressures.

* Translated by Earl C. Gregg, Jr. for Rubber Chemistry and Technology from *Kauchuk i Rezina* 17, No. 3, 5–11 (1958).

** M. P. Potapenko, O. N. Setkina, A. A. Ryabkova, G. P. Sokolova, A. S. Shirkevich and L. K. Gaifman participated in the experimental part of the work.

TABLE I

VARIATION OF PROPERTIES OF SKB RUBBER WITH CONDITIONS OF THERMAL TREATMENT

Name of product	Shore hardness	Density, g/cm³	Solubility in chloroform, %	Equilibrium swelling in benzene, %	Temperature of decomposition, ° C	Unsaturation, %
Control rubber SKB	—	0.913	completely	soluble	295	97.8
SKB after 4.5 hours at 10,000 kg/cm² and 240°	95	1.056	0.9	9.0	392	13.8
SKB with 240 hours in air at 240°	95	1.044	1.0	17.3	355	72.7

The chemical vulcanization of raw rubbers under high pressures does not appear in the literature. The present work is dedicated to the study of chemical curing of raw rubber under high pressures and also to the explanation of the action of the various components of a rubber compound.

It is known that during vulcanization several competing crosslinking reactions take place simultaneously. High pressure, besides accelerating reactions and guaranteeing monolithic rubber, must also displace the equilibrium in the direction of the arrangement for maximum compression, that is, to favor the formation principally of the stable carbon-carbon crosslink. The control of the formation of carbon-carbon bonds in vulcanization is very important because they are associated with an increase in the thermal and chemical stability of vulcanizates.

We studied the curing of different gum rubbers and rubber compounds under pressures of 3000–10,000 kg/cm² and at temperatures of 120–200°. Samples (cylinders 25 mm in diameter and thin wafers 50 mm in diameter) were made up in a 120 ton vulcanization press with the help of special plunger forms. For investigation of curing and evaluation of properties the prevailing methods as well as certain elaborations and adaptions of them[21,22] were used.

CURE OF GUM RUBBER

Natural and synthetic rubbers heated under high pressure acquire properties characteristic of commercial vulcanizates in spite of the absence of vulcanizing agents. Their toughness, hardness and resilience increase and consequently their swelling and solubility[23] decrease. The variation of properties of SKB rubber is represented in Figure 1.

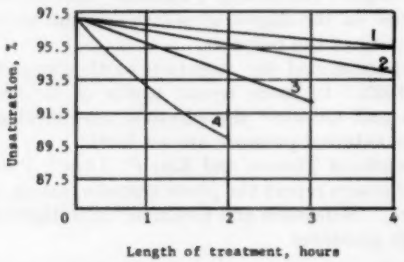

FIG. 2.—Variation of unsaturation of SKB rubber with length of treatment at various temperatures and pressures (bromination in the vapor state): *1*—160° at 5 kg/cm², *2*—180° at 5 kg/cm², *3*—160° at 5000 kg/cm², *4*—180° at 5000 kg/cm².

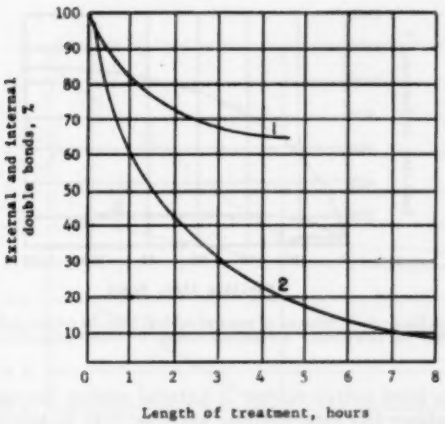

FIG. 3.—Variation of internal and external double bonds of SKB rubber depending on length of treatment at 10,000 kg/cm² and 160° (infrared spectral data): *1*—internal double bonds, *2*—external double bonds.

The action of high pressures on rubbers has an effect similar to the action of radiation[24]. With an increase of pressure, molecules of rubber interact in a manner not observed at ordinary pressures.

The resulting products of cure of SKB rubber (Table I) are substantially different from the usual thermal vulcanizates of SKB.

The difference in the amount of unsaturation of comparable materials makes it impossible to demonstrate the acceleration of the reaction brought about by pressure. In the polymer oxygen crosslinks apparently prevail at the alpha-methylenic group[25].

By a study of the structure of products from SKB cured under high pressure it is established that there results primarily an opening of the double bonds and the consequent formation of carbon-carbon crosslinks (Figure 2). During this cure the external double bonds of the rubber react more rapidly than the internal double bonds (Figure 3); their increased activity perhaps is explained by less steric hindrance under high pressure.

Experiments with other rubbers at high pressures yield additional proof of the predominant participation in the vulcaizationn by the external double bonds (Figures 4, 5 and 6).

Judging from the rate and degree of cure of rubbers, SKB rubber possesses the greatest reactivity because it contains the greatest amount of external

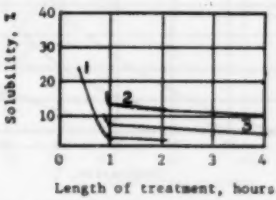

FIG. 4.—Variation of solubility in chloroform of natural rubber, SKS-30 and SKB depending on the length of treatment at 10,000 kg/cm² and 160°. *1*—SKB rubber, *2*—natural rubber, *3*—SKS-30 rubber.

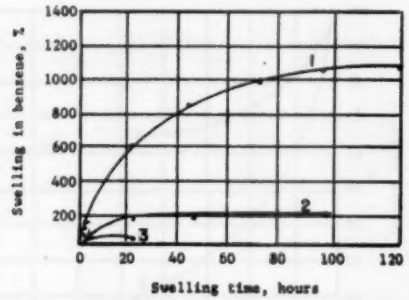

FIG. 5.—Variation of swelling rate in benzene of natural rubber, SKS-30 rubber and SKB rubber at 10,000 kg/cm² and 160° for two hours. *1*—natural rubber, *2*—SKS rubber, *3*—SKB rubber.

double bonds; the least active rubber is natural rubber because it has no such bonds; SKS-30 rubber has intermediate activity. If to this is added the fact that rubbers having low unsaturation (butyl rubber and polyisobutylene) under the same conditions of test show no detectable change, it is possible to establish these two conditions: a) cure of gum rubbers is defined by unsaturation and is accomplished at the expense of the double bond b) more reactive rubbers are characterized by a higher percentage of external double bonds.

However, high pressure activates internal double bonds of rubber and because of this it was possible for the first time to prepare a "pure vulcanizate" of natural rubber and also a series of crosslinked block polymers from natural rubber and SKB rubber which have interesting properties.

CURE OF COMPOUNDED RUBBERS

The fundamental part of the present work is devoted to the explanation of the action of the different components of a rubber compound. First of all we consider the action of the vulcanization agent, sulfur, on the cure of rubbers under high pressure.

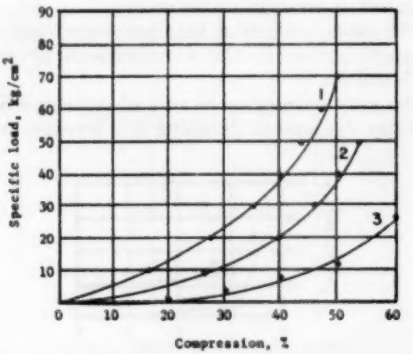

FIG. 6.—Variation of compression of natural rubber, SKS-30 rubber and SKB rubber depending on length of treatment at 10,000 kg/cm² and 160°. *1*—SKB rubber (for 1 hour); *2*—SKS-30 rubber (for 1 hour), *3*—natural rubber (for 2 hours).

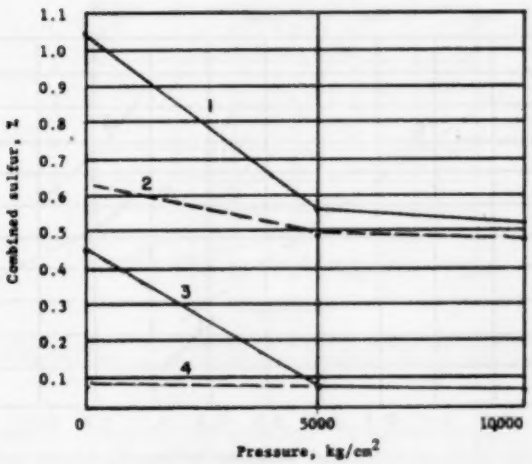

FIG. 7.—Bound sulfur in SKB rubber as a function of pressure (cure at 160°): *1*—Cure time 1 hour; SKB-100 g, sulfur-2.5 g, *2*—Cure time 0.5 hour; SKB-100 g, sulfur-2.5 g, *3*—Cure time 1 hour; SKB-100 g, sulfur-0.5 g, *4*—Cure time 0.5 hours; SKB-100 g, sulfur-0.5 g.

In the same fashion as in the case of gum rubber an increase of pressure accelerates and increases the state of cure of the rubber-sulfur mixture. However, the action of sulfur itself on SKB rubber under high pressure is markedly reduced (Figures 7 and 8). With a stepwise increase of pressure the state of cure of rubber increases (solubility, swelling etc. decrease) and the amount of bound sulfur decreases. The decrease of the effect of the vulcanizing agent and the increase of the reactivity of the rubber under the conditions of high pressure was established with the series of compounds of SKB[26] rubber and may be seen in Figure 9.

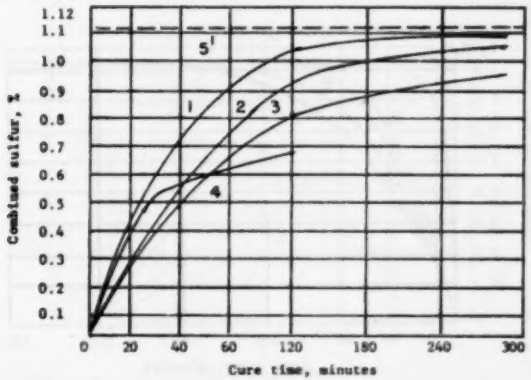

FIG. 8.—Bound sulfur of a black loaded compound of SKB rubber as a function of cure time at 160° and various pressures: *1*—5 kg/cm², *2*—3000 kg/cm², *3*—5000 kg/cm², *4*—10,000 kg/cm², *5*—maximum amount of combined sulfur.

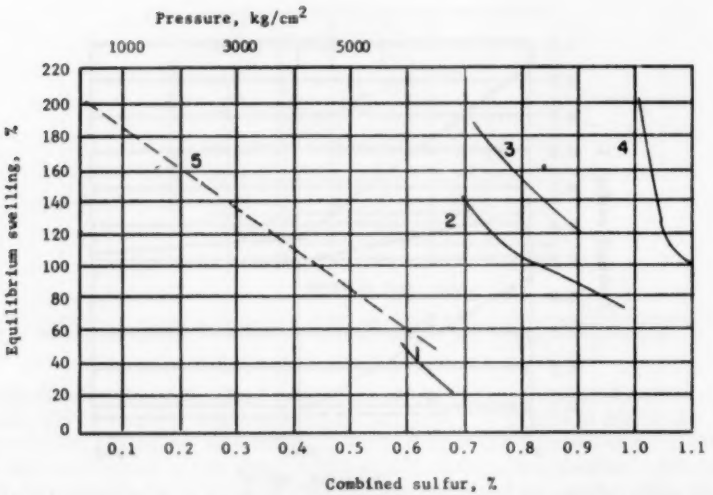

FIG. 9.—Relationship of equilibrium swelling and combined sulfur of black loaded SKB rubber as a function of vulcanization pressure at 160°. *1*—10,000 kg/cm², *2*—5000 kg/cm², *3*—3000 kg/cm², *4*—5 kg/cm², *5*—swelling as a function of pressure at a constant amount of combined sulfur in rubber (0.9%).

On the left side of this figure the dotted straight line (according to swelling data) shows that with an increase of pressure the overall crosslink density increases in vulcanizates containing a constant amount of combined sulfur (0.9%). In regard to this then this figure shows the general displacement of the curved lines (drawn for four states of cure) from the right downwards to the left, i.e., in the direction of decreased swelling and decreased content of combined sulfur with an increase of vulcanization pressure.

Under the condition of high pressure the crosslinking reaction predominates without participation of the vulcanizing agent in such a way that it allows a greater compression of the structure with resulting excellent physical properties

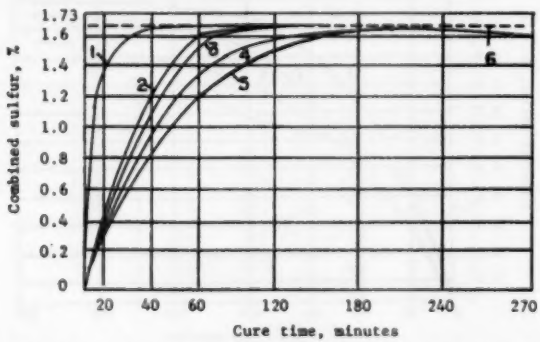

FIG. 10.—Combined sulfur of natural rubber depending on cure time at 160° and various pressures: *1*—ordinary vulcanizate, *2*—3000 kg/cm², *3*—5 kg/cm², *4*—5000 kg/cm², *5*—10,000 kg/cm², *6*—limiting amount of combined sulfur.

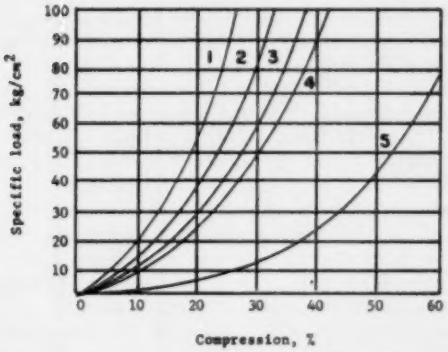

FIG. 11.—Relation of compression of rubbers on type of filler during treatment of SKB compounds at 10,000 kg/cm² and 160° for 1 hour; *1*—carbon black, *2*—magnesium oxide, *3*—lamp black, *4*—silica, *5*—chalk.

similar to those of commercial vulcanizates. In particular some vulcanizates of SKB rubber prepared at 10,000 kg/cm², if judged by their stability toward solvent action, approach the specialty rubbers for this purpose.

High pressure exerts another action on vulcanization of rubbers containing sulfur. In the case of natural rubber it inhibits only the initial rate of sulfur combination but has almost no effect on the total amount of bound sulfur (Figure 10).

In contrast to vulcanizates from SKB rubber a vulcanizate from natural rubber is formed mainly at the expense of the sulfur content of the crosslinks and judging from its behavior it resembles vulcanizates formed at ordinary pressure. Results of study of compounded natural rubber under pressure agree with results of study of gum natural rubber. The behavior of compounded butyl rubber is similar to the behavior of compounded natural rubber.

The resulting data show that the basic cause of the unusual behavior of sulfur in the vulcanization of SKB rubber under pressure appears to be in-

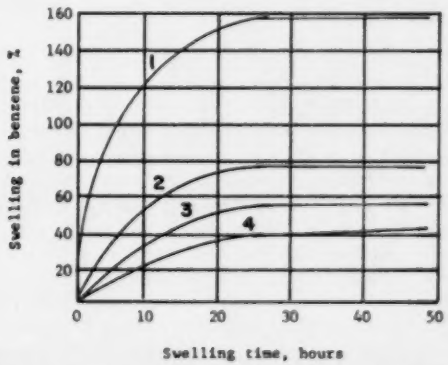

FIG. 12.—Relation of swelling of rubber in benzene with type of filler of SKB compound at 10,000 kg/cm² and 160° for 1 hour: *1*—chalk, *2*—silica, *3*—magnesium oxide, *4*—lamp and gas black.

creased reactivity of the rubber and the decreased reactivity of the sulfur because of an increased viscosity of the rubber and melting point of sulfur and a consequent decrease of its diffusion.

The action of types of ingredients of rubber compounds on cure under pressure was also studied. A comparison of the action of different active fillers and softeners (Figures 11, 12 and 13) shows that the effect of these components, in contrast to sulfur, does not undergo substantial change. In the same manner as under the usual conditions of cure of rubber these fillers and softeners give the vulcanizate its requisite quality. Gas black assists the formation of tough rubbers which are resistant to solvents. Among the softeners the most useful proved to be dibutyl phthalate which provides resilient rubbers with satisfactory resistance to solvents. By employing high pressure and the beneficial nature of the individual agents vulcanizates may be obtained which contain no vulcanizing agents but which have the requisite gamut of properties required for resilient and tough vulcanizates.

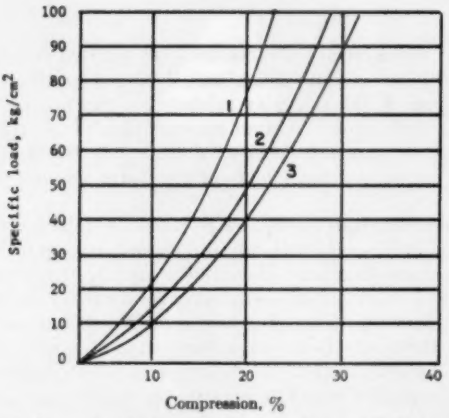

FIG. 13.—Relation of compression of rubber with type of softener of SKB compound at 10,000 kg/cm² and 160° for 1 hour: *1*—asphalt, 5 parts by weight (and original mixture), *2*—stearic acid, 5 parts by weight *3*—dibutyl phthalate, 5 parts by weight.

Experiments of curing of sodium-butadiene rubber in the presence of inhibitors and initiators (PBNA, benzoyl peroxide and others) show that such additives substantially influence the speed and extent of reaction (Table II).

It may be speculated that benzoyl peroxide, when decomposed, promotes the formation of stable high molecular weight radicals which accelerate the vulcanization of rubber. PBNA, on the other hand, destroys the resulting radicals and inhibits the process. With the presence of benzoyl peroxide in the rubber compound the cure of comparatively thick samples is completed in 1–3 minutes which has a definite technical advantage.

Cure of rubber under pressure may be compared with polymerization of monomers and permits the study of how free radical processes are initiated by heat. In the act of initiating such a reaction two molecules of rubber can be involved to form a biradical[27]. Therefore, higher pressure will accelerate not only the crosslinking but initiation. With an increase of pressure the viscosity

TABLE II

INFLUENCE OF ANTIOXIDANT AND BENZOYL PEROXIDE ON THE CURE OF SKB RUBBER UNDER HIGH PRESSURE

	Rubber	Conditions of treatment	Solubility in $CHCl_3$, %	Equilibrium swelling in benzene, %
1	Original SKB rubber	30 min at 160° and 10,000 kg/cm²	3.8	280
2	SKB free of antioxidant	30 min at 160° and 10,000 kg/cm²	1.7	101
3	Original SKB rubber with 3 g of PBNA per 100 g of rubber	30 min at 160° and 10,000 kg/cm²	80	soluble
4	Original SKB rubber and 3 parts of benzoyl peroxide	45 min at 200° and 5 kg/cm²	13.8	509
5	Original SKB rubber and 3 parts of benzoyl peroxide	Treatment in two stages: heating for 10 min at 5 kg/cm²; 1 min extra at 200° and 10,000 kg/cm²	3.1	73.8
6	Original SKB rubber and 1 part of benzoyl peroxide	Treatment in two stages: heating for 10 min at 200° and 5 kg/cm²; extra 3 min at 200° and 10,000 kg/cm²	8.7	251

of the medium increases due to which the scission reaction is inhibited which appears to be one of the causes of the acceleration reaction.

High pressure which accelerates the interaction of rubber molecules, may also promote compression and physically a more uniform vulcanizate of improved quality (without pores, flaws etc.).

The statement regarding appearance applies to other rubbers under the action of high pressure. Further development of these studies may be interesting not only for establishing more precise mechanisms of vulcanization, but also for solving some practical problems. In particular the use of high pressure may directly convert SK rubbers (modified by lignin or other additives) into new products and eliminate all the complex intermediate technological operations.

Superfast curing of rubber compounds without vulcanizing agents affords an opportunity to combine the continuous processes of stamping and vulcanization.

It is clear that these and other possible technological methods of treatment of rubber are not suitable for all rubber articles, but their use for the production of certain rubber articles is quite possible. The cumbersome arrangement necessary for the development of high pressure requires special installations for production of rubber vulcanizates. In this connection the works of engineer L. A. Yutkina are of definite interest because of his practical use of the electrohydraulic effect for creating high pressure impulses[28].

SUMMARY

1. The influence of high pressures (up to 10,000 kg/cm^2) on the cure of gum and compounded rubbers and also on the properties of the resulting products was studied.

2. It was demonstrated that high pressure accelerates vulcanization and effects the specific formation of stable carbon-carbon crosslinks. Thus, crosslinked polymers may be prepared without any vulcanizing agents, yet the resulting vulcanizates have excellent properties. New methods were designated for obtaining crosslinked block polymers having stable crosslinks.

3. It was determined that cure depends on the reactivity of the rubber, the type of unsaturation and, most important, the amount of spatially more accessible external double bonds.

4. It was shown that during the cure of rubber compounds under high pressure the participation of sulfur in the formation of the vulcanizate is substantially decreased. In a mixture of SKB rubber and sulfur the dominating reaction is the interaction of molecules of rubber. Functional fillers and softeners do not undergo substantial change. The use of initiators of radical polymerization contributes by leading to ultrarapid vulcanization of rubber.

5. An assumption is stated concerning the mechanism of vulcanizing rubber under high pressure as well as certain questions about the use of high pressure as a new method of producing molded rubber articles.

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DIFFUSION OF SULFUR IN RUBBER IN RELATION TO VULCANIZATION *

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The present work is a report concerning the diffusion of sulfur in rubber. Following a suggestion of Prof. W. Seith, it was originally planned to investigate only the diffusion of radioactive, bound sulfur. If such a diffusion took place at all, it would seem to be equivalent to a wandering of the sulfur bridges which crosslink the carbon chains of the polymerized isoprene molecules in the vulcanizate and impart elasticity to the rubber. However, since the sulfur bridges are not exactly defined, and other types of combined sulfur can be present in the rubber, such a conclusion is not quite justified. Before such measurements are undertaken, one should be familiar with the diffusion of *free* sulfur in the rubber. Furthermore, a possible thermodynamic equilibrium between the free and the bound sulfur might invalidate the measurements. It was thus necessary to first determine the possibility of the occurrence of this equilibrium as well as the rate at which it is established. The diffusion experiments made it mandatory that suitable analytical procedures be found.

Because of the multiplicity of the procedures, methods, and results, it appeared to be desirable to subdivide the material to be presented into several sections. First there will be a compilation of literature dealing with the chemistry of vulcanization.

THE CHEMISTRY OF RUBBER VULCANIZATION

As is known, natural rubber is essentially a polyisoprene:

$$\left[\begin{array}{c} -CH_2-C=CH-CH_2- \\ \quad\quad\quad | \\ \quad\quad\quad CH_3 \end{array}\right]_n$$

with n = 5000 to 50,000 or higher[1]. Basically, two possibilities exist for the binding of sulfur during vulcanization: first the formation of an intermolecular sulfur bridge between the carbon chains[2,50]; secondly, an intramolecular sulfur binding to the individual carbon chains[2]. Under the influence of sulfur, furthermore, a cyclization or polymerization of the rubber molecule chains should be possible, leading to a crosslinking of two C=C double bonds, without any sulfur being combined[2]. In addition a dehydrogenation effect of sulfur in vulcanizations is known[17].

That the formation of bridges between two rubber-hydrocarbon chains leads to vulcanization has been shown in a number of studies, reviewed by van Alphen[1]. In addition to sulfur, other vulcanization agents can be used, e.g., the dithiols HS—R—SH, among others. That the vulcanizing action of elemental sulfur is attributable principally to the formation of bridge bonds, is

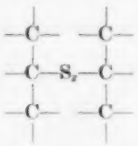
* Translated for RUBBER CHEMISTRY AND TECHNOLOGY by G. Leuca from *Kautschuk und Gummi*, Vol. 12, pages WT 59–68, March 1959.

apparent from a rather large number of studies by Selker and Kemp[58,59], Bloomfield[9], as well as Farmer and Shipley[18,19,21].

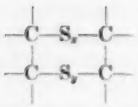
From the elongation modulus of vulcanizates and their susceptibility to swelling in organic solvents, the number of sulfur bridges formed can be calculated. It turns out that in a nonaccelerated vulcanization reaction the greater part of the sulfur does not contribute to bridge formation, but is consumed in the formation of intramolecular rings and is hence lost for any vulcanization purposes. Furthermore, it has been shown by the x-ray investigations of Meyer, Ferri, and Hohenemser[41] that this ring sulfur can be detrimental to the properties of the vulcanizates.

The question is raised as to how many atoms there are in a sulfur bridge. From the decrease in the number of double bonds, determinable analytically[51], and the quantity of bound sulfur, one can calculate the length of the sulfur bridges. Zapp and coworkers[73] indicate there are 1.2 to 31.8 sulfur atoms per bridge, with 2 atoms per bridge in the case of good vulcanizates and low vulcanization temperatures. This number is also given by Hauser and Sze[28], as well as by other authors. At higher temperatures the S—S bonds are ruptured and the bridges are unstable[28,74]. Investigations by Selker and Kemp[56] show that even the heat treatment and access to air which occur when vulcanizates are extracted to determine the free sulfur can lead to a change in and a degradation of these bridges. The latter authors were also able to establish the occurrence of polysulfide bridges in the reaction with sulfur of a model substance, namely 2-methyl-2-butene. Here prolonged heating also leads to a splitting off of sulfur from the polysulfide bridges. This sulfur reacts with the double bonds still present[57].

Up to now the nature of the sulfur bridges was implicitly assumed to be the result of the addition of sulfur onto a semiruptured double bond of a molecule and at a corresponding spot at another molecule. When one bond of a double bond is ruptured, reaction possibilities result at two neighboring C atoms, so that not only the following simple bridge can occur:

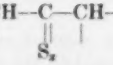


but also a double one[13]:



It is further possible that the unsaturated portions of the reacting double bonds of the two chains produce a C—C bond:

The formation of thioketones



with model substances has been reported by Kambara and Ohkita[29]. Information pertaining to other reaction products can be found in articles by Hauser, Sze and Brown[27,28]. Van Amerongen and Houwink[2] have eliminated a number of the numerous possibilities for steric reasons.

Just as numerous as the reaction products are the reaction mechanisms discussed in the literature. Bloomfield[8], as well as Farmer and Shipley[19], for example, regard the radicals—both sulfur and carbon radicals—to be intermediate products. Van Alphen[1] disputes this possibility, at least for accelerated vulcanizations. Williams[71] showed that after peptization of vulcanizates, fractions varying in sulfur content can again be precipitated.

According to Boggs and Blake[10] vulcanization commences each time at the end of a molecule, at a double bond, as a soft-rubber vulcanization. When the bound sulfur content reaches 0.5%, the soft-rubber vulcanization should be over. This corresponds[11] to a composition: $(C_5H_8)_{200}S_2$. Nowadays we assume 2–3% bound sulfur as the limit for soft-rubber vulcanization. In support of this limit there are, among other things, the data supplied by Blake[6], that up to 4–6% of bound sulfur, essentially no heat of reaction is encountered.

After the soft-rubber vulcanization phase is over, sulfur is added intramolecularly to the double bonds of a chain, whereby the reaction progresses, in succession, from one end of the chain to the other[10,26,28]. Passage through the leathery stage leads to hard rubber or ebonite. According to Kemp and Malm, up to a composition $(C_5H_8S)_n$ there is taken up 32% by weight of sulfur = 47 parts of sulfur to 100 parts of rubber.

Attempts to establish the occurrence of polysulfide bridges in ebonite, such as is possible in soft rubber[11,58,59] were, of course, unsuccessful because no polysulfide bridges should be present in ebonite, due to their sensitivity to prolonged heating during vulcanization.

That the sulfur combined by rubber is in part only very labilely bound is also shown by exchange reactions and interactions between vulcanizates, (radioactive) sulfur, and accelerators. In this connection one can cite articles by Langenbeck[36], Krebs[35], and Blokh[6,7].

The processes become even more complicated when one takes into consideration the numerous modifications of elemental sulfur. Reference can be made to the comprehensive articles about sulfur by Schenk[53] and Fehér[20]. What interests us here is not the multiplicity of crystalline modifications of sulfur, but the transformations and equilibria in the liquid phase.

Freshly molten rhombic or monoclinic sulfur consists of S_λ, representing nonplanar S_8 rings. After a while an equilibrium is established with S_π, which has a molecule size of $S_4 \cdots S_8$. S_π can be isolated as a highly viscid to oily mass, and then slowly changes to S_μ. S_μ consists of molecular chains of varying lengths. If highly-heated sulfur is suddenly quenched, one obtains a plastic S_γ, which in turn consists of S_λ and S_μ. The equilibrium relations between these modifications are complex.

The variation in chemical reactivity of sulfur under different molecular conditions is not surprising. Fehér cites work which describes μ-sulfur as an insecticide or fungicide, superior in its effectiveness to normal sulfur. In

addition, he refers to a patent by Endres[15], according to which the portion of plastic sulfur (i.e. $S\mu$) which is insoluble in carbon disulfide is more suitable for vulcanization than normal sulfur.

Nordlander[43] showed that the rate of vulcanization, over a wide range of temperature, is directly proportional to the $S\mu/S_\lambda$ equilibrium in a sulfur melt. We shall return to his important work, to which little attention has been paid in the literature.

ANALYTICAL METHODS

In the experiments to be described, in order to determine the total sulfur content we used decomposition by combustion[69] with subsequent nephelometric titration of the sulfate formed[68], both procedures as given by Wickbold. In the Wickbold combustion apparatus the combustion gases from a rubber sample are conducted through a oxyhydrogen flame into a solution of hydrogen peroxide

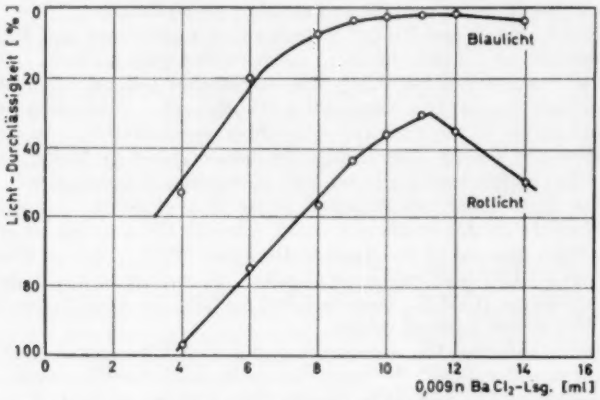


FIG. 1.—Turbidity titration of sulfate with barium chloride solution. Abscissa: 0.009 *N* $BaCl_2$ solution (ml); ordinate: light permeability (%); Blaulicht = blue light; Rotlicht = red light.

so that all of the SO_2 is oxidized to SO_3. The sulfuric acid which is formed is titrated with barium chloride solution with addition of suitable electrolytes. Up to the point of equivalent concentration the solution will become increasingly turbid, until, with the addition of excess barium chloride solution it becomes clearer again. Ringbom[49] and Frey[21] had already described a similar procedure.

Certain changes were made as compared to the original Wickbold procedure: titration was with 0.01 *n* $BaCl_2$ solution. When the sulfate content was over 0.8 mg S, 10 ml of distilled water was added to the titration solution as given by Wickbold. The work was carried out with a Zeiss flicker photometer (without a nephelometric attachment). Lower sulfate contents were titrated with blue filter S42, higher ones with red filter S75. The advantage of red light titration in the case of larger quantities of sulfate is shown in Figure 1. All in all, sulfate quantities of 0.2···3.2 mg S per test sample can be titrated with no difficulty.

There were insufficient amounts of material available in the diffusion experiments to determine the free sulfur according to the sulfite or acetone extraction method. For this reason the Proske procedure was used[46]. The

rubber sample was extracted with pyridine and the sulfur was determined polarographically in an aliquot portion of the extract—without regard for the possible solution of weakly-vulcanized samples in pyridine. The sample for analysis should contain 0.1 to 0.8 mg S, but even 10γ can be determined, and, with reduced accuracy, 0.2γ/10 ml of solution. It should be stated that the procedure indicated by Proske was later perfected by Poulton and Farrant[44]. Attention should be called to the work of Proske for the polarographic determination of accelerators[47,48].

Only very small amounts of material are required for the above-mentioned analytical methods. To obtain an average value, larger samples were frozen in liquid nitrogen and then chipped off with a drill press.

The decomposition of samples containing radioactive sulfur S_{35} was accomplished with sodium peroxide in a combustion bomb, according to the method of Professor Wurzschmitt.

KINETICS AND THERMOCHEMISTRY OF THE VULCANIZATION REACTION

The work of Skellon[61] and Spence and Young[62,63] should be mentioned as among the earliest studies reporting on the rate of decrease in the free sulfur content of sulfur/rubber mixtures as a function of the time. The authors found that the amount of bound sulfur, x, over a number of hours, is proportional to the time, t. This linearity is lost only after a rather long period of time. The authors determined the ratio $k = x/t$ for different temperatures. The values of k are dependent on the initial sulfur concentration.

The temperature coefficient of the vulcanization reaction was calculated from two k values for different temperatures. Williams[70], and also Selker and Kemp[67] later found a constant reaction rate for a model substance, namely 2-methyl-2-butene. According to this, the reaction between sulfur and rubber would be of zero order.

Gordon[22], however, calculated from experiments by Zapp and Ford[74] that the vulcanization reaction was of the first order with respect to the sulfur. Van Alphen[1] eliminated the discrepancy by explaining that the reaction is of zero order as long as the rubber is saturated with sulfur, i.e., as long as undissolved sulfur is still present.

Values for the temperature coefficient of the vulcanization reaction are given by Kemp and Malm[32] as well as by Kemp and Ingmanson[31].

A general description of the reaction course would be given by the Arrhenius equation:

$$k = a \cdot e^{-Q/RT} \tag{1}$$

The frequency factor a, however, has up to now been given only by Gordon for Buna S and Springer[64] for natural rubber.

The heat of activation, Q, has been given frequently, e.g., by Nordlander[43], Gordon[22,23], Auerbach[3], Meyer (reference 6 in reference 23) and Springer[64]. The values vary between 27,000 and 35,600 cal for natural rubber; they are of the same order of magnitude as the heat necessary to split an S_8-ring. This has been given as 27.5 kcal by Powell and Eyring[45] and should represent the predominant portion of the activation energy of vulcanization[64].

Unfortunately all of the authors cited hardly distinguish between soft rubber and hard rubber vulcanization. Special studies attempting to describe the two types of reactions have been made by Lewis, Squires and Nutting[37].

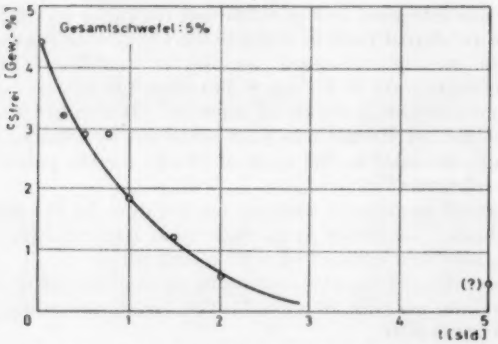


FIG. 2.—The combination of free sulfur as a function of the time in the vulcanization of crepe rubber at 150° C. Abscissa: time in hours; ordinate: $c_{S\,free}$ (per cent by weight); Gesamtschwefel = total sulfur.

Moreover, these authors, as well as Bruce, Lyle, and Blake[14] established that the combination of the first percentages of sulfur occurs without any appreciable heat of reaction.

Experimental method.—A number of samples of sulfur-rubber mixtures prepared on the mill were vulcanized in an electrically-heated aluminum block for various times at different temperatures (135° and 150° C). Three series of experiments were conducted each time, with 5%, 12.8% and 19.3% or 20% total sulfur. After different reaction times, the free sulfur still present was determined according to the procedure which has been previously described.

Results.—Equation (2) shows the most general formulation of a mathematical description of the reaction rate

$$v = -\frac{dc_{S\,free}}{dt} = k' \cdot c_{S\,free}{}^{m} \cdot c_{C=C}{}^{n} \qquad (2)$$

In this equation v is the reaction rate, c the corresponding concentration and t the reaction time. k' is a constant. The decrease in free sulfur with the time, i.e. the reaction rate of the vulcanization, is thus proportional to a con-

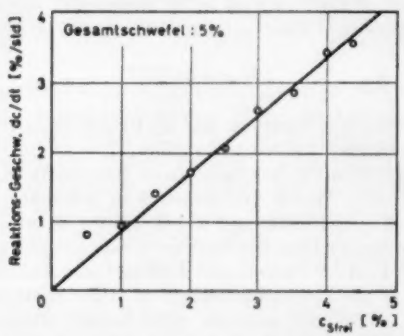


FIG. 3.—Dependence of the reaction rate on the concentration of the free sulfur in the vulcanization of crepe rubber at 150° C. Abscissa: $c_{S\,free}$ (%); ordinate: reaction rate dc/dt (%/hours).

stant factor and to some still undetermined power of the concentration of free sulfur and of the double bonds. If it is postulated that 1) the reaction rate v is either independent of the number of double bonds, or the number of double bonds—when small amounts of sulfur are present—does not decrease to any appreciable extent, that 2) the reaction runs in a monomolecular way with

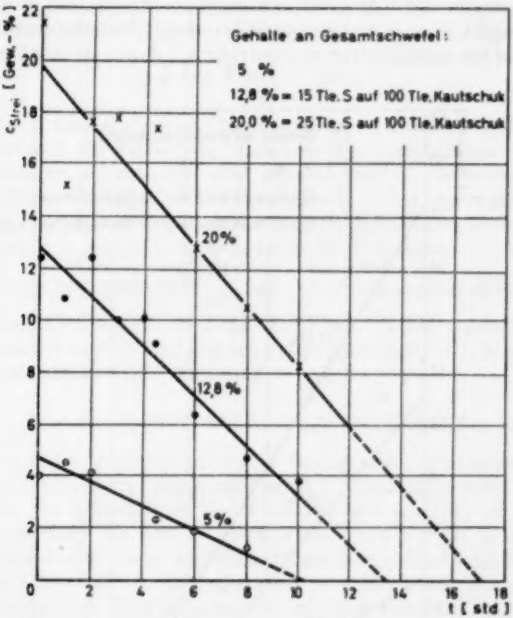


FIG. 4.—The combination of free sulfur as a function of the time in the vulcanization of crepe rubber at 135° C and with different total sulfur contents. Abscissa: time in hours; ordinate: $c_{S\,free}$ (per cent by weight). Overall sulfur contents: 5%; 12.8% = 15 parts S to 100 parts rubber; 20.0% = 25 parts S to 100 parts rubber.

respect to the sulfur ($m = 1$), and that 3) the total sulfur is dissolved in the rubber from the beginning of the reaction, Equation (2) transforms into the simpler form of Equation (3):

$$c_{S\,free} = c^{\circ}_{S\,free} \cdot \epsilon^{-kt} \tag{3}$$

in which $c^{\circ}_{S\,free}$ is the initial concentration of free sulfur.

When the initial sulfur concentration is 5% and the reaction temperature 150° C, the course of the reaction can actually be described by an exponential function (Figure 2). Accordingly, the reaction rate $v = -dc_{S\,free}/dt$ is directly proportional to the concentration of free sulfur $c_{S\,free}$ present at any time (Figure 3). The slope of the straight line in Figure 3 is given by the reaction constant k of Equations (1) and (3).

$$k_{423^{\circ}K} = 0.014\ [\text{min}^{-1}]$$

At higher sulfur concentrations or lower temperatures, i.e. whenever the total free sulfur does not dissolve immediately in the rubber, Equation 3 no longer holds true.

The results of other experimental series are given in Figures 4 and 5. The curve from Figure 2 is included in Figure 5. It appears here as approximating a straight line. The scattering in many of the series of measurements stems from an inhomogeneity of the initial material. The curves in Figures 4 and 5 appear as straight lines in the region of interest. But the reaction rate is not independent of the initial sulfur concentration. A simple mathematical formu-

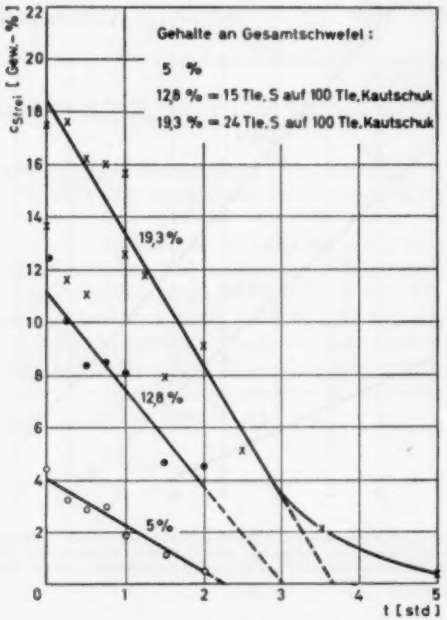


FIG. 5.—The combination of free sulfur as a function of the time in the vulcanization of crepe rubber at 150° C and with different total sulfur contents. Abscissa: time in hours; ordinate: $c_{S\,free}$ (per cent by weight). Overall S contents: 5%; 12.8% = 15 parts S to 100 parts rubber; 19.3% = 24 parts S to 100 parts rubber.

lation of reaction kinetics does not satisfactorily explain the situation. Apparently the reason is to be found in the fact that the undissolved sulfur according to the amount in which it is present in the rubber represents a variable reservoir for the more reactive μ-sulfur (cf. the theory of Nordlander[43]).

Despite the difficulty of comprehending the relations quantitatively, it is possible, from the results presented in Figures 4 and 5, to calculate the activation energy of the vulcanization reaction. It lies in the range 34.1 to 35.7 kcal, depending upon whether one uses the experimental series with 5%, 12.8% or 20.0% total sulfur for the calculation. The average value is

$$Q = 34.8 \text{ kcal}$$

The series with 5% total sulfur thus provided the same value for the activation energy as the more highly sulfurated series. Apparently both soft rubber and hard rubber vulcanizations require approximately the same activation energy (provided that the soft rubber vulcanization is carried out to appreciable sulfur contents, at least 2 to 3%). This again makes it plausible that the major portion of the activation energy must be supplied to the sulfur.

After the values for k and Q in Equation (1) are known, the frequency factor a of this equation can also be computed:

$$a = 4.4 \times 10^{16}\ [\text{min}^{-1}]$$

This value is almost the same as that given by Gordon for Buna S vulcanization ($2 \cdot 10^{13}$ to $2 \cdot 10^{16}$ [min^{-1}]). However it is quite different from the value cited by Springer for unaccelerated natural rubber vulcanization ($3.3 \cdot 10^{-13}$ [min^{-1}]). (Note the signs of the exponents!) This discrepancy shows that it is not meaningful to attribute quantitative significance to the values of the frequency factor, a, which have thus far been determined.

The temperature coefficient, $\frac{dv}{dT}$, of the vulcanization reaction can be derived in different ways from the data obtained. At our experimental temperatures it amounted to 2.65 (for a temperature rise of 10° C), in good agreement with the values found in the literature.

DIFFUSION OF SULFUR IN RUBBER

Ever since the adsorption theory of vulcanization was abandoned and the vulcanization reaction was recognized to be a chemical process, references have been made in the literature to the solubility and mobility of the free sulfur. Weber was probably the first to identify the phenomenon as diffusion. Loewen[38,39] was the first to cause sulfur to diffuse into rubber with heat; after cooling the sample he observed the separation of sulfur under the microscope. A later publication by Morris[42] provided an experimental improvement over Loewen's simple microscope investigations. Skellon[60,61] discovered that the sulfur diffuses out of rubber samples into those with lower sulfur concentrations. He used this method to determine the solubility of sulfur in rubber. Skellon recognized the fact that the diffusion of sulfur occurs rapidly and vulcanization much more slowly.

For a long time these processes were not measured. The method was used merely for studying the solubility of sulfur in rubber, especially with regard to the homogeneity of the vulcanizates (Venable and Green[67], Kelly and Ayers[30]). The latter authors were the first to determine that the mobility of the sulfur decreases with increase in degree of vulcanization. They also determined that its solubility increases with the degree of vulcanization, which, to be sure, is not directly related to the central theme of this work, but had to be considered in evaluating our own diffusion experiments.

The "blooming" of sulfur on the surface of rubber articles is not possible without the diffusion of the sulfur. This phenomenon shows in addition, that this diffusion is appreciable even at room temperature. This problem has been discussed by Graffe[24] and Endres[16]. Endres obtained a patent for vulcanization with a sulfur product enriched in S_μ, through the use of which blooms were presumably eliminated, especially in vulcanized raw stock in storage[15].

The studies which have been cited describe the diffusion of sulfur only from

a qualitative standpoint. Quantitative diffusion measurements were first carried out with other materials. In particular, the water sorption and permeability of rubber were measured, and also the gas permeability[52,72,66,61,65].

Grün[25] investigated the diffusion of different organic compounds. He showed that the diffusion coefficient (D in $cm^2 \cdot sec^{-1}$), for compounds and gases with molecular weights between 2 and 1086 decreases with rising molecular weight in about linear fashion. Of interest also is the fact that the mobility of low molecular weight materials in rubber is smaller by only about one power of ten than in an aqueous solution. A comparison of the diffusion coefficients given by Grün with our own for sulfur is not possible because of the temperature difference. Yet it can be said that according to our measurements a diffusion of the sulfur in the atomic state would not be in accord with Grün's table, but certainly such would be the case for the diffusion of a polyatomic sulfur modification, say S_8 or a higher polymer.

Kemp, Malm, Winspear and Stiratelli[34] investigated the adsorption and diffusion of sulfur in a temperature range of 25 to 96° C. They packed rubber samples in powdered sulfur. Even at a temperature of 25° C the amounts of sulfur taken up after 300 hours were quite considerable. A 0.5 mm thin crepe sheet took up, during this time, 2.88% of its weight in sulfur. The same amount was also taken up at 56° C. The present author also has found a reaction limit between 2 and 3% in his diffusion experiments. An interpretation of this will be given later. Kemp and coworkers also made the first attempt to set up a concentration penetration curve (c-x curve; c = concentration, x = distance of this concentration from the original sulfur-rubber interface). In this, they did not distinguish between free and bound sulfur, apparently because, at 56° C, they expected no vulcanization, even after 500 hours. The penetration depth reached after this time was 2.5 cm and the limiting surface concentration, about 2%. The foregoing authors conducted their principal experiments according to another method; they allowed sulfur to pass through a rubber membrane and determined the loss in weight of the "diffusion cell." They established that the diffusion rate is gradually reduced with the time, and that it also decreases with increase in the degree of vulcanization. Kemp, Malm and Stiratelli[33] treated the diffusion of sulfur in Buna in another publication. The diffusion rate is lower than in crepe.

Auerbach and Gehman for the first time used radioactive sulfur, S_{35}, to determine the solubility of sulfur in rubber[4]. In addition they calculated the diffusion coefficients (40° C, $D = 0.5 \cdot 10^{-7}$ $cm^2 \cdot sec^{-1}$; 60° C, $D = 2.5 \cdot 10^{-7}$ $cm^2 \cdot sec^{-1}$). For Buna S, they found values that were about 50% higher. The activation energy for diffusion is given as 17 kcal.

The work of Bresler, Prjadilowa and Chainman[12] is especially noteworthy. They investigated the diffusion of sulfur at temperatures that are also technologically interesting, namely at 130° to 150° C. Their method was similar to that of Gehman and Auerbach, since they applied the radioactive sulfur to one side of thin rubber disks and followed the increase of the radioactivity of the other side of the disks during diffusion. They found a diffusion coefficient $D = 0.194$ to $1.61 \cdot 10^{-6}$ $cm^2 \cdot sec^{-1}$. The activation energy of the diffusion was indicated to be 7000 ± 100 cal/mol.

Experimental method.—The rubber samples used in the diffusion experiments were first cut out roughly from Defo sheets, placed in the diffusion mold and heated under a ram pressure so that they became plastic and adhered to the sides of the mold. After cooling, the rectangular test piece was removed from the mold. The surface of the specimen was freshly finished on a microtome.

Then the specimen was placed in the mold again together with a likewise exactly fitting rectangular block of sulfur. A coarse porous glass frit was melted into the small block of sulfur. The apparatus was tightly sealed on top with a sheet of vulcanized rubber free of accelerator and pressed together with a tightly-fitting metal piston by means of a pressure spring. The side walls were sealed with Araldit synthetic resin. The whole arrangement is illustrated in Figure 6. This apparatus was then fitted, quite tightly, into an electrically-heated aluminum block, which moreover, to eliminate oxygen, was flushed continuously with a stream of nitrogen. Everything was arranged so that the specimens could be heated up quickly, and also cooled quickly after the experiment. The cooled specimens, when taken from the mold were frozen in liquid nitrogen. After removal of the outside layers they were mounted in a deeply cooled clamping device and cut up on the microtome into layers 30 to 50μ in thickness under

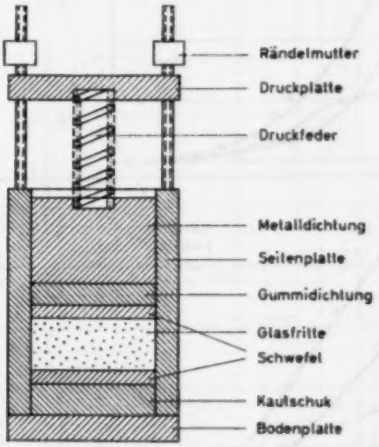
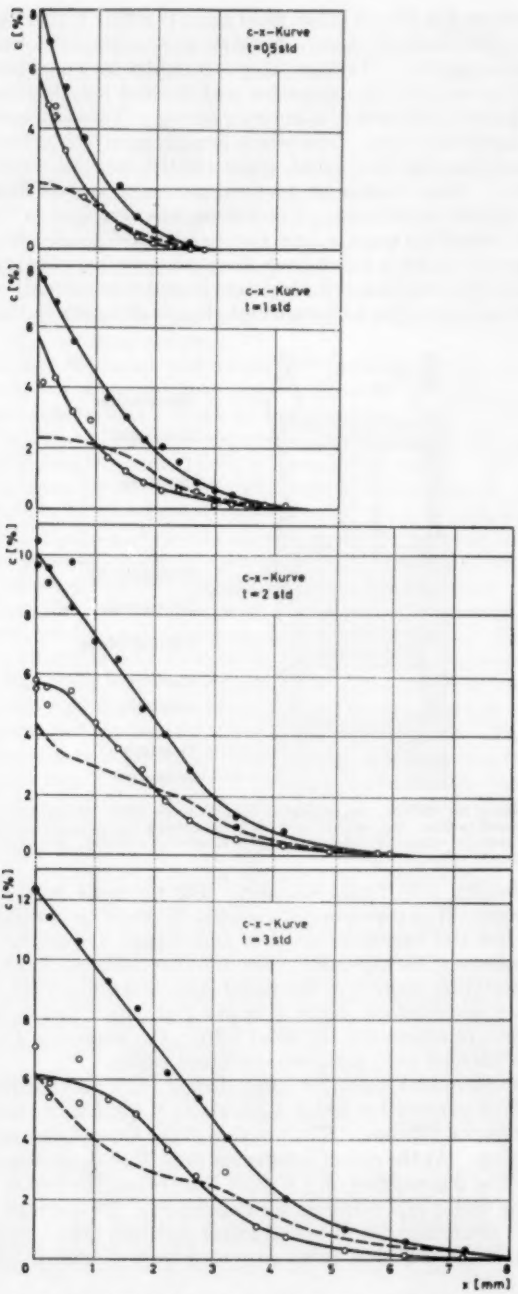


FIG. 6.—Apparatus for diffusion experiments. Rändelmutter = nut; Druckplatte = pressure plate; Metalldichtung = metal packing; Seitenplatte = side wall; Druckfeder = pressure spring; Gummidichtung = rubber packing; Glasfritte = glass frit; Schwefel = sulfur; Kautschuk = rubber; Bodenplatte = base plate.

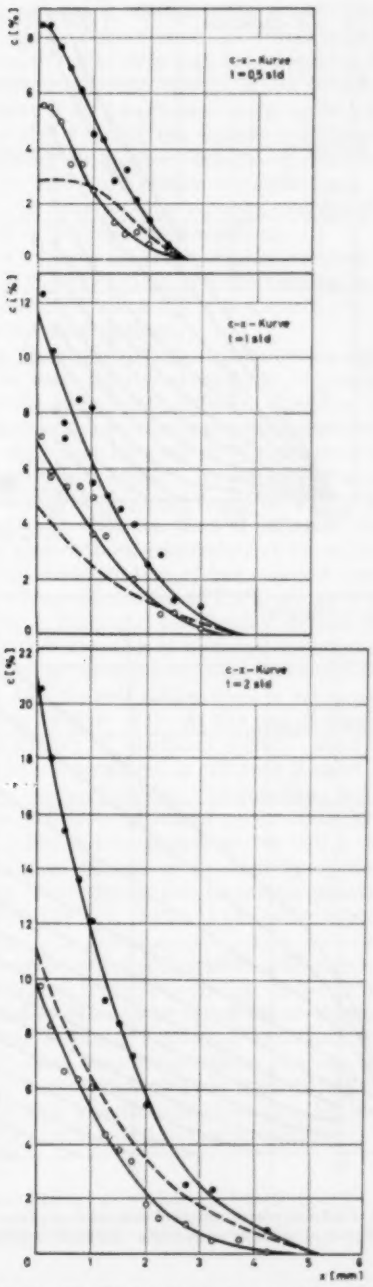
continuous spraying with liquid nitrogen. For the most part, every 5 or 10 sections was regarded as a section for analysis, in which, according to the cited methods, the free and overall sulfur were analytically determined.

Time-dependence of the diffusion.—For different diffusion times and temperatures the penetration depth x of the sulfur concentration c will be represented graphically as a so-called c-x curve (Figures 7 to 13). In the diagrams, the upper curve always represents the total sulfur, the lower one the free sulfur. The difference (dashed line) gives the combined sulfur.

None of the c-x curves, taken by itself, displays any peculiarities, except for the large depth of penetration which amounts to a number of millimeters after only one half hour of diffusion. The position of the curves with respect to each other is surprising. At the end of a diffusion zone, that is, at deep penetrations x, which the sulfur has reached only a short time before the end of the diffusion experiment, one would expect free sulfur exclusively. But instead of this it was revealed that a predominance of bound sulfur occurred here. One is forced to assume the preferred diffusion of an activated form of sulfur. Actually it is



FIGS. 7–10 (from top to bottom).—The diffusion of sulfur in crepe rubber (100% S in 100% crepe) when T = 135° C and t = 0.5 hours, 1 hour, 2 hours, and 3 hours. Kurve = curve; Std = hrs.



FIGS. 11–13 (from top to bottom).—The diffusion of sulfur in crepe rubber (100% S in 100% crepe rubber), when T = 150° C and t = 0.5 hours, 1 hour and 2 hours.

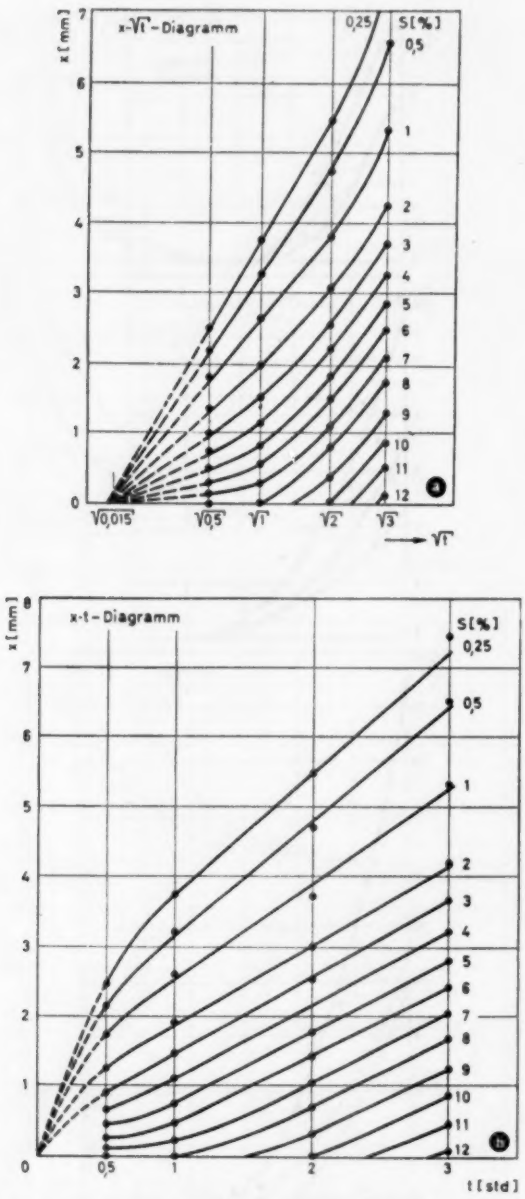


FIG. 14.—Penetration depth of different concentrations of total sulfur as a function of the time. (Figure a: $\sqrt{t}$; Figure b: t) for the diffusion of sulfur in crepe rubber (100% S in 100% crepe), when T = 135 C°.

easy to imagine that S_τ or even S_π chains diffuse much more rapidly in rubber than S_λ rings. In the other diffusion zones, too—that is, at low x values—vulcanization took place much faster than was to be expected from the investigations of reaction kinetics with sulfur/rubber mixes prepared on mills. This rapid vulcanization proceeds with particular speed up to a content of 2 to 3% bound sulfur. This limit of 2 to 3% has already been encountered elsewhere. Hence there is the tendency to suppose that this is connected with a limit or boundary between soft- and hard-rubber vulcanizations. The hard-rubber vulcanizations, too, in our diffusion experiments, run faster than normal, but not as vigorously as the soft-rubber vulcanizations.

The solubility of free sulfur at the sulfur/rubber interface ($x = 0$), is derived from the c-x curves. When the extent of vulcanization is 2%, the solubility of the free sulfur is about 5.5%; at 6.1% it is about 6.1%. These values are lower than those given by other authors.

Further information about the diffusion phenomenon is obtained when the penetration depth, x, for each given concentration, c, (c is taken as the parameter) is plotted against the appropriate diffusion time t, or against $\sqrt{t}$. From such diagrams, of which only the one for total sulfur is reproduced here (Figure 14), one can recognize that: only for very short times does the diffusion follow the so-called "law of parabolic increase," according to which, for a constant c, the penetration depth x should be proportional to $\sqrt{t}$. Furthermore it turns out that: almost immediately after the start of diffusion, the concentration of 2% of bound sulfur has already been established at the sulfur/rubber interface. In addition the solubility concentration of free sulfur is reached very quickly, so that a concentration of the total sulfur of 7.5% occurs in the boundary layer ($x - 0$) almost from the beginning. For further details reference should be made to a more complete presentation of these investigations[40].

Temperature dependence of the diffusion.—Also at a diffusion temperature of 150° C (Figures 11, 12, 13), the soft rubber limit is indicated again as between 2 and 3% of bound sulfur (Figure 11). At the end of the diffusion zone there is once again a preponderance of combined sulfur. With increase in experimental time, however, the development is different than at 135° C: because of the higher temperature the hard rubber vulcanization is more strongly promoted and considerable quantities of bound sulfur occur in the total diffusion area. This directly diminishes the amount of free sulfur remaining. On the other hand this free sulfur is hindered in its mobility by the increasing degree of vulcanization. As a consequence, the maximum penetration of sulfur at 150° C is less than that at 135° C! More of the sulfur is bound in the vicinity of the boundary surface.

Diffusion coefficient and the energy of activation.—The literature (e.g., Seith[55]) should be consulted in regard to the calculation of the diffusion coefficient D (according to the method of Matano or by means of the Gaussian error integral). Calculation of the diffusion coefficient according to one of the cited methods leads only to formal values, because of the overlapping of diffusion and chemical reaction. Such values must be regarded as approximations because of the variable solubility of sulfur and other variable boundary conditions.

As approximate values for a diffusion temperature of T = 135° C, one obtains, for

Total sulfur: $D = 3.5 \cdot 10^{-6}$ ($cm^2 \cdot sec^{-1}$)

Free sulfur: $D = 2.2 \cdot 10^{-6}$ ($cm^2 \cdot sec^{-1}$)

These values are in good agreement with those of Bresler and coworkers[12]. It can be shown that the values arrived at are smaller—because of the complicated circumstances—than would correspond to the true mobility of the sulfur. The error grows larger with the temperature and the duration of the diffusion. The formal diffusion coefficient D is consequently found to be scarcely dependent on the concentration. Also it depends only inappreciably on the temperature.

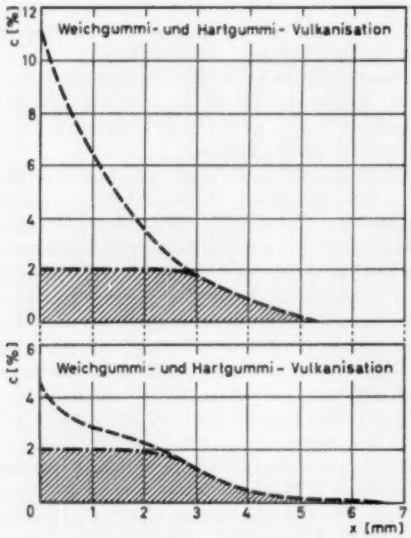


FIG. 15.—The $c - x$ curve for combined sulfur for the diffusion of sulfur in crepe rubber (100% S in 100% rubber) when T = 150° C (above) and 135° C (below) and t = 2 hours. Weichgummi = soft rubber; Hartgummi = hard rubber.

By means of very special considerations, in spite of the difficulties involved, a value can be obtained for the true energy of activation of the diffusion of *free* sulfur from the c-x curves for two temperatures. Thus the activation energy for the diffusion of free sulfur amounts to about

$$Q = 8000 \text{ (cal/mol)}$$

Bresler gives 7000 cal/mol. If Auerbach and Gehman[4] found 17 kcal, that may be true for their experimental temperatures (40° C and 60° C), but for 130° C this value is decidedly too high.

If one calculates the formal activation energy for the diffusion (even if it is only formal), of the *bound* sulfur, then one should expect a value which corresponds approximately to the activation energy of the vulcanization reaction. Actually a much lower value is obtained. However, if one takes into consideration with c-x curves (Figure 18), the zone which corresponds approximately to soft rubber vulcanization with the already pre-activated sulfur modification, then the activation energy for the hard rubber vulcanization can, in fact, be estimated from these curves to be about 28 kcal/mol, approximately, which is of the expected order of magnitude. In doing this we assumed that the re-

action, up to the limit of 2% bound sulfur, would not require any appreciable addition of activation energy. This assumption is all the more justified, since the mechanism by which the accelerators work is to depress the energy required to split the S_8 rings. The fact that ultra accelerators[10] can promote vulcanization even in the cold is explicable only by assuming a strongly reduced activation energy. Furthermore, attention should be called to cold vulcanization with sulfur chloride, S_2Cl_2. Cold vulcanization can also take place with $H_2S + SO_2$ (reference 2 in reference 43). In doing this one need not bring the rubber directly in contact with the gases, but can use plastic sulfur precipitated from the gas phase. In all these cases, the sulfur is likewise present in a state that scarcely requires any supplemental addition of activation energy (to the sulfur or to the rubber), in order to achieve soft rubber vulcanizates.

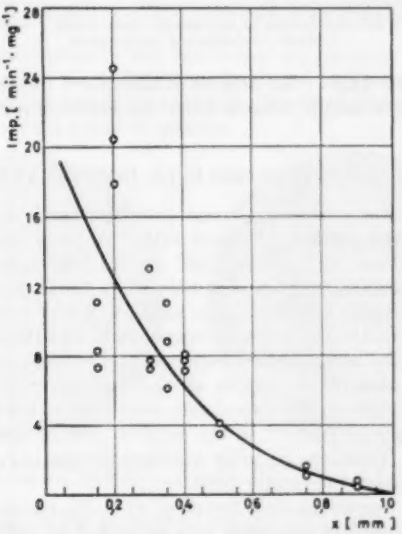


FIG. 16.—Migration of radioactive sulfur from a vulcanizate prepared with 835 into one containing nonradioactive sulfur. X = penetration depth of S-35 into the originally nonradioactive portion of the sample.

Theory of Nordlander.—Nordlander[42] in his work, already mentioned, shows that the vulcanization rate increases with the temperature to the same extent as does the S_μ content of a sulfur melt. Attempts of authors cited by Nordlander to prove the difference in the vulcanization rates for S_λ and S_μ through the use of pure modifications have up to now not had the desired success, perhaps because the conversion $S_\mu \rightleftharpoons S_\lambda$ takes place too quickly. (In regard to the preparation of pure sulfur modifications see Reference 25 in Reference 20).

It seems all the more valuable to the present author that the diffusion experiments which have been described lead indirectly to the same opinion as that put forward by Nordlander, namely that a certain sulfur modification (apparently S_μ) contained in the sulfur melt is particularly suited for vulcanization.

This view does not entirely agree with that of Meyer (Reference 14 in Reference 64) according to which the conversion $S_\lambda \rightarrow S_\mu$ leads to an especially

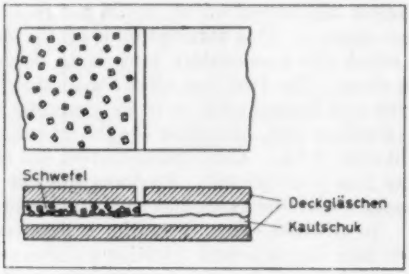


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FIG. 17.—Arrangement of a diffusion sample for microscopic observations. Schwefel = sulfur; Kautschuk = rubber; Deckgläschen = cover glass.

reactive intermediate stage. An argument advanced for this latter theory is the fact that hydrogen sulfide retards both the conversion $S_\lambda \rightarrow S_\mu$ and the rate of vulcanization.

MIGRATION OF SULFUR CROSSLINKS DURING VULCANIZATION

Experimental method.—Two mixtures with the same sulfur content were prepared: a) 100 parts rubber, 15 parts sulfur, 5 parts titanium dioxide (as colorant): vulcanization, 51 hours at 150° C. b) 100 parts rubber, 15 parts sulfur, 3 parts red iron oxide (glowed mostly to Fe_3O_4 at over 1450° C). This mixture was milled to give a thin sheet, a solution of S35 in anisole was applied to it (1.5 mc. of S35), the solvent was evaporated, and the sheet was homogenized on the mill. By using certain experimental techniques, a 3.3 cm^2 slab, 2 mm thick, was vulcanized (conditions as given in a), and freshly cut on the surface with a microtome. The specimen was then extracted with acetone. Radioactive material was present in the extract, but no free elemental sulfur could be detected. Testpiece b) after vacuum drying gave 50,000 to 60,000 counts per minute under the Geiger tube.

Testpiece b) was pressed against testpiece a) in the boxlike mold previously described and the complete specimen was subjected to diffusion in the usual manner; conditions: 5 hours at 135° C. Subsequently the testpiece was

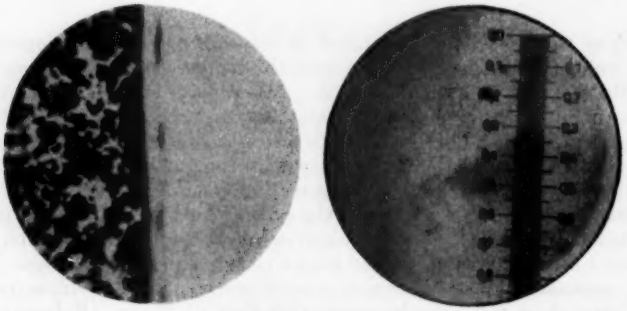


FIG. 18.—Microscopic view of a sample of the type shown schematically in Figure 17. The dark portions are powdered sulfur. Next to it is a millimeter scale.

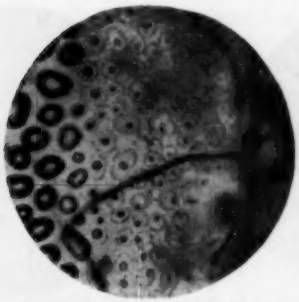
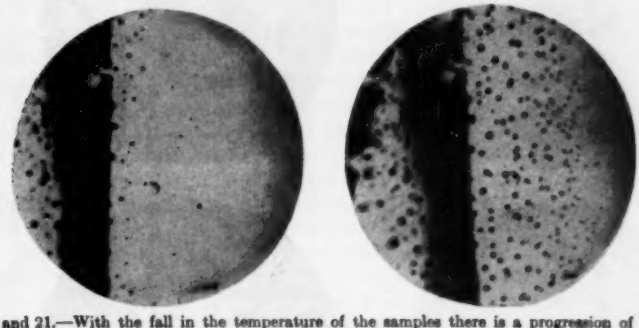


FIG. 19.—The left-hand portion of Figure 18 after heating and diffusion during cooling of the sample. The first deposits of (noncrystallin) sulfur are visible at the edges of the disappearing sulfur droplets.

sectioned with the microtome. The individual layers were sealed in a bomb with sodium peroxide, and the sulfate thus produced (with the addition of more sulfur) was precipitated as benzidine sulfate. The benzidine sulfate was placed under the Geiger tube in a suitable manner.



FIGS. 20 and 21.—With the fall in the temperature of the samples there is a progression of the sulfur precipitate in the direction of lower sulfur concentrations.

Results.—In Figure 16 the number of counts in the individual layers of the initially inactive testpiece a) are plotted against the distance from the boundary surface, $x = 0$ (i.e., boundary surface of testpiece a) against testpiece b)). The number of counts obtained from the starting material (testpiece b)), namely

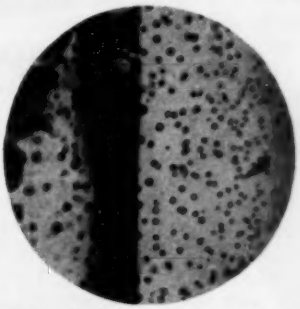
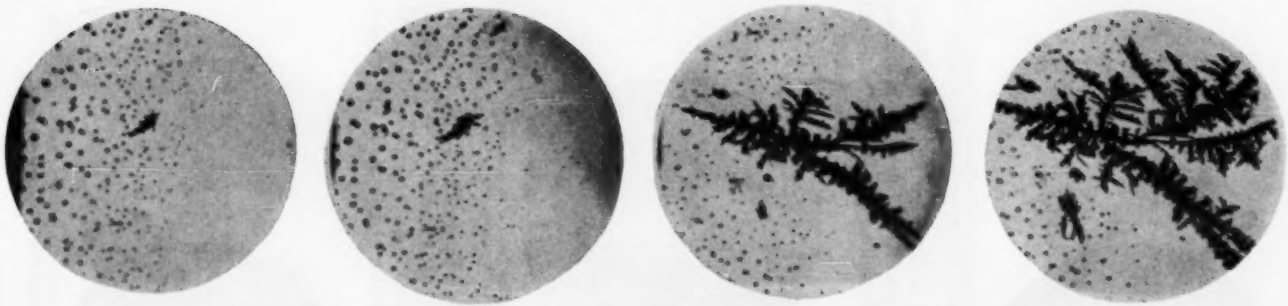


FIG. 22.—A crystal nucleus in the originally sulfur-free diffusion zone.



FIGS. 23-26.—Growth of the crystal nucleus into regions in which there is no further droplet separation.

FIG. 27.—Dendritic crystal growth, beginning with a droplet nucleus. As soon as a droplet is reached by a dendrite branch, it becomes a new crystalization center. Crystal modification: presumably rhombic.

FIG. 28.—Featherlike sulfur crystals, also beginning at droplets. Crystal form: presumably monoclinic.

FIG. 29.—Rhombic and monoclinic sulfur precipitates. Para-spots can be seen around the rhombic form.

FIG. 30.—Transformation of monoclinic sulfur into the rhombic form with crystal growth, after allowing the sample to stand for several days.

2000 counts per mg per min may be used for comparison. The diffusion effect is thus very slight. It can in nowise be attributed to wandering free sulfur or wandering sulfur bridges, but to the diffusion of S35-containing compounds formed during vulcanization and not removed quantitatively by the subsequent acetone extraction.

The result is thus: in thoroughly vulcanized rubber containing 15 parts of sulfur to 100 parts of rubber, in which polysulfide bridges are presumed not to occur, no exchange of the bound sulfur can be proved (excepting for a purely physical migration of low molecular weight sulfur compounds). Bresler and coworkers found an effect in polysulfide-containing vulcanizates. This is not a contradiction of our results.

MICROSCOPE OBSERVATIONS

A description of the sulfur diffusion processes occuring in rubber would be incomplete without reporting purely phenomonological investigations, which however in principle add nothing new, having already been carried out in a similar way by Loewen[38,39] and Morris[42].

Experimental method.—Solutions of rubber in carbon tetrachloride and acetone were dried on glass slides. Powdered S was introduced into one half of the sample. Such a test object is represented schematically in Figure 17. The preparations were heated for some time under a microscope with a hot stage at about 150° C and were then cooled.

Results.—Figure 18 shows a test preparation before being heated. Upon heating the sulfur melts into droplets and partially diffuses into the rubber. Cooling at first causes the sulfur to precipitate on the original edges of the now shrunken or disappearing droplets, Figure 19. (The fibrous foreign body does not belong in the picture). With further cooling, the sulfur precipitation proceeds into zones with lower sulfur content (Figures 20 to 22). Precipitation first occurs in the form of droplets, which later become centers of crystallization (Figures 22 to 27). The rhombic form of sulfur must be involved in this precipitation (according to Loewen). Figure 28 shows the precipitation of monoclinic sulfur; Figure 29 both modifications with para-spots around the rhombic form. After a few days the finely branched monoclinic modification transforms into larger rhombic crystals (faintly recognizable in Figure 30). For such a process a diffusion of sulfur is once again required, although it is not a volume diffusion, but a pure surface diffusion along the crystals which are present. The rate of conversion proved to be dependent on the medium bounding the sample, since the transformation of the crystals was retarded by the cover glass which was applied. This might be attributed to the stress strain conditions in the rubber film. In contrast to this, no sulfur precipitation was observed upon cooling a sample vulcanized at 180° C.

ACKNOWLEDGMENTS

The author is indebted to the late Professor W. Seith for encouragement to undertake this work, and for helpful discussions. Professor Theodor Heumann is to be thanked for valuable advice. *Chemische Werke Hüls AG* in Marl, and the Rubber and Plastics Division of *Farbenfabriken Bayer Aktiengesellschaft* at Leverkusen as well as the *Battelle Memorial Institute*, German branch, in Frankfurt/Main, placed apparatus, materials and financial means at my disposal to assist with the investigations. For this, too, the author wishes to express his gratitude.

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VULCANIZATION OF ELASTOMERS. 28. VULCANIZATION OF NATURAL AND SYNTHETIC RUBBERS WITH SULFUR IN THE ABSENCE OF ACCELERATORS. I *

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INTRODUCTION

In several previously published papers[1] we investigated the kinetics of sulfur concentration decrease in accelerated vulcanizations of NR as well as of synthetic rubbers; we developed the view that there are several vulcanization processes which have common characteristics with respect to decreasing sulfur concentration[2]. These results are based on broad experimental investigations and should be of value in the elucidation of the mechanism of the vulcanization reaction and also they would be of interest to the process engineer. The results may be summarized:

1. There are a number of practical vulcanization processes in which sulfur concentration decrease follows 0.7 to 0.8th order kinetics independent of temperature and concentration of reactants (sulfur and accelerators). The reason for the fractional order, with respect to time, may be the catalytic effect of reaction products (crosslinks with polysulfide structure), in other words, the decrease in sulfur concentration is probably an autocatalytic process[3].

2. This was observed in the following vulcanizations: a) vulcanization of NR and synthetic rubber in the absence of organic bases, b) the vulcanization of Perbunan, and possibly other poly-1,3-dienes in the presence of sulfenamids, c) vulcanizations accelerated by mercaptobenzothiazole in the presence of ZnO[4], and e) vulcanizations accelerated by benzothiazolyl disulfide when certain molar ratios of sulfur and accelerator prevail.

3. In these vulcanizations, a discrepancy in the reaction order is usually observed with respect to reaction time and concentration of reactants[2,5]. They may not only be due to the autocatalytic decrease in sulfur concentration, but also be due to the appearance of intermediates, which are formed in a fast reaction and form an equilibrium mixture with sulfur and accelerator. These intermediates may be the real vulcanizing agents.

This assumption is based on the experience that the relation between starting rate of decreasing sulfur concentration and the starting concentration cannot be described by a single exponential law; it is generally found that the starting rate increases rapidly at low reactant concentration and becomes constant at higher concentrations; this is the case when sulfur concentration is constant and accelerator concentration is varied as well as in the case of varied sulfur concentration and constant accelerator addition. It may, therefore, be assumed that the reaction order discrepancy mentioned before has possibly two

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY by O. C. Elmer from *Kautschuk und Gummi*, Vol. 12, Pages WT 233 to 239. Two tables of data have been omitted to save space.

causes. If one could expect, because of the autocatalytic nature of the sulfur disappearance, that the dependence of the starting rate of the sulfur starting concentration would follow a different law than the decrease of sulfur concentration with time, it would still seem plausible that these dependent functions could not be described with one continuous exponential law becuase of the appearance of intermediates. One concludes from the kinetics of sulfur decrease in an accelerated vulcanization that the process is very complex. It occurred to us that one could clarify the situation by studying the kinetics of sulfur disappearance in the vulcanization process in the absence of any additives; the results should then be compared with those obtained from the accelerated vulcanizations.

In the past, the reaction of sulfur with gum rubber, so called "pure sulfur vulcanization", has been investigated extensively. From Springer's[6] critical survey and summary of results published up to about 1945, we gather that the decrease of sulfur concentration is supposed to be of zero order throughout a wide concentration and temperature range[7] while it is 1st or 0.8th order with respect to the starting concentration of sulfur[8,9]. It is difficult to discuss the material compiled by Springer in detail, since it is the result of the work of many experimenters and incomplete in parts; it could, however, be clearly established that a discrepancy exists in reaction order with respect to time and concentration even in the absence of additives. Nevertheless, we repeated measurements of the sulfur decrease in "pure" sulfur vulcanization, since we wanted to explain the results obtained from the various investigators.

EXPERIMENTAL RESULTS

Starting material for all experiments was NR (pale crepe) exhaustively extracted with acetone. For the quantitative determination of unreacted free sulfur, the vulcanizates, obtained in the usual way, were extracted with a benzene/alcohol (2:1) mixture at room temperature. When the solvent is renewed repeatedly, the extraction is finished in about eight days. The extracts were combined in a volumetric flask and made up to a definite volume. Aliquots of this solution were boiled with 25% aqueous sodium sulfite after the solvent was removed, whereby thiosulfate equivalent to the amount of sulfur present, is formed. After addition of an excess of a 40% formalin and acidification with acetic acid the solution was titrated with a standard iodine solution[10].

First we investigated the influence of temperature on decreasing sulfur concentration; each 100 g of gum rubber compound contained 12.5 mmoles S_8. Table I (omitted from this translation) contains the results of experiments performed at 140, 145, 150, 153.8 and 160°. A plot of the amount of sulfur remaining in the extracts versus reaction time showed, that the sulfur decrease neither occurs according to the first or zero order at any of the temperatures investigated. A thorough analysis of the conversion curve gave $n = 0.6$ for the reaction order. Consequently it was shown that a fractional reaction order of the decreasing sulfur concentration results when pure sulfur vulcanization takes place with a starting sulfur concentration of 12.5 mmoles S_8 (3.2%) in 100 g. of compound, assuring complete solubility of the sulfur in rubber in the temperature range investigated. The same thing had been observed in the case of accelerated sulfur vulcanization, but the reaction order in that case was somewhat higher with values between 0.7 to 0.8[2]. Figure 1 shows the correctness of the calculated reaction order. There the values obtained from the integration of the differential equation for the reaction of the nth order $1/1(S_0 - S_t)^{1-n}$

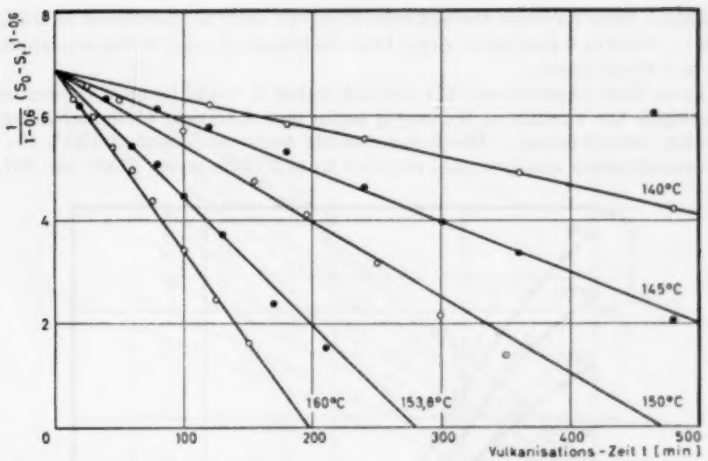

FIG. 1.—Decrease of sulfur concentration according to the 0.6th order for the reaction of NR with sulfur at different temperatures $(S_0) = 12.5$ mmoles in 100 g compound. Ordinate: $1/1-0.6(S_0 - S_t)^{1-0.6}$. Abcissa: Vulcanization time t (min).

using the value $n = 0.6$ were plotted against vulcanization time (S_0 = starting sulfur concentration, S_t = amount reacted). It can be seen that straight lines are formed as it should be for the 0.6th reaction order. If one plots the log of the rate constants of the 0.6th order calculated from the slopes in Figure 1 against the reciprocal absolute temperature, the straight line in Figure 2 is

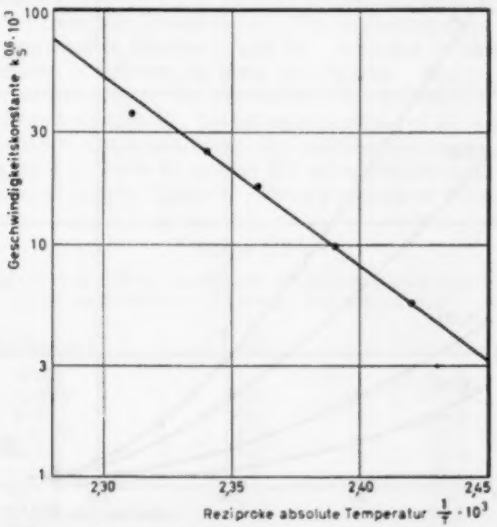

FIG. 2.—Temperature dependence of the 0.6th order rate constant of sulfur decrease in the reaction of NR with sulfur $(S_0) = 12.5$ mmoles in 100 g compound. Ordinate: Rate constant $k_S^{0.6} \cdot 10^3$. Abcissa: Reciprocal absolute temperature $1/T \cdot 10^3$.

obtained; from its slope the activation energy may be calculated as 35 kcal/mole. It is 5 to 6 kcal/mole larger than for the accelerated sulfur vulcanization (28 to 30 kcal/mole).

From these experiments it is concluded that it would be most interesting to investigate the kinetics of decreasing sulfur concentration while increasing the starting concentration. These experiments were conducted at 150°; the sulfur concentration was increased stepwise from 3.125 mmoles (0.88) per 100 g of

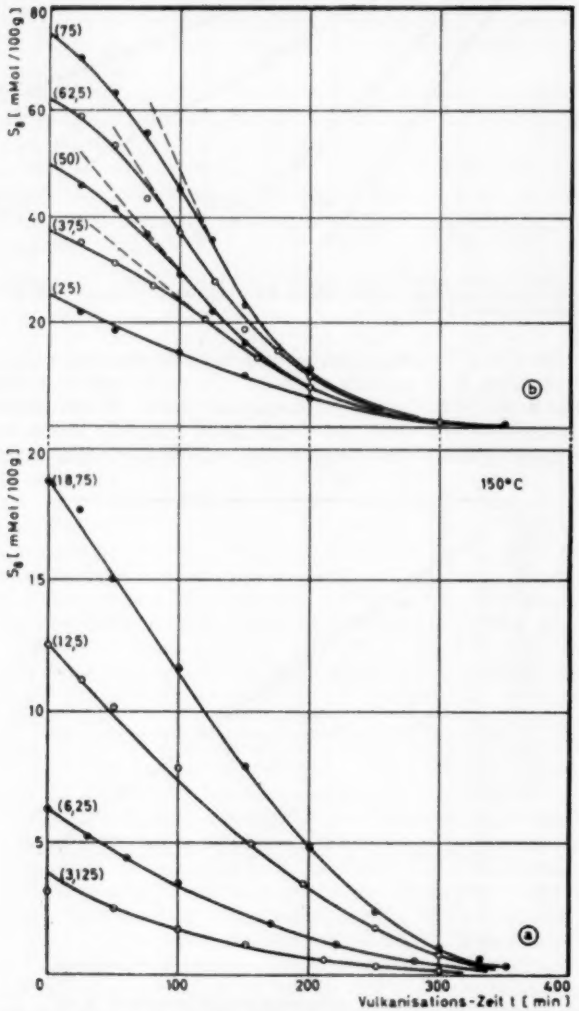

FIG. 3.—Decrease in sulfur concentration in the reaction of NR with sulfur. T = 150°; numbers in parenthesis are starting concentrations of sulfur in mmoles S_8 in 100 g of compound. Ordinate: S_8 [mmoles /100 g.]. Abscissa: Vulcanization time t (min.).

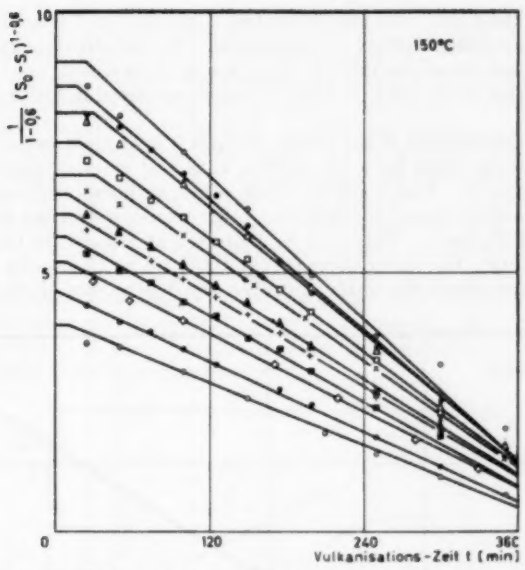

FIG. 4.—Decrease of sulfur concentration according to the 0.6th order at different starting concentrations at 150°. $(S_8)_0$ in sequence of the curves from the lowest upward: 3.125, 4.687, 6.25, 7.813, 9.375, 10.938, 12.5, 15.625, 18.75, 21.875, and 25.0 mmoles in 100 g compound. Ordinate: $1/1-0.6(S_0-S_t)^{1-0.6}$. Abscissa: Vulcanization time t (min.).

compound to 75 mmoles S_8 (19.2 g.). The experimental results are tabulated in Table II (omitted from this translation). The important data from Table 2 are graphically presented in Figures 3a and 3b. It should be observed that the scale of the ordinate is different in these two figures. The conversion plots show convex curvature toward the abscissa at 150° and in the concentration range from 3.125 to 25 mmoles S_8. By taking an average of all values, a reaction order value $n = 0.6$ is again obtained. By plotting the values of $1/1-0.6(S_0 - S_t)^{1-0.6}$ (Column 4 in Table 2) against the vulcanization time, straight lines are again obtained as seen in Figure 4. From the slope of these lines the rate

TABLE III

RATE CONSTANTS FOR 0.6TH ORDER AND STARTING RATES FOR THE SULFUR VULCANIZATION OF NATURAL RUBBER AT 150°

$(S_8)_0$ [mmoles]	$k_r^{0.6} \cdot 10^3$ $(n=0.6)$	$[d(S_8)/dt]_0 \cdot 10^3$
3.125	10.0	19.8
4.6875	11.5	29.1
6.25	12.5	37.5
7.8125	13.7	47.1
9.375	14.5	55.5
10.9375	15.5	65.1
12.5	17.5	79.5
15.625	18.6	96.78
18.75	20.0	116.2
21.875	21.4	136.3
25.0	23.0	159.0

constants for the 0.6th order are calculated (Column 2 in Table III), which increase with increasing starting concentration. By substituting rate constants and starting concentrations into the time law as determined, one can calculate the starting rates $[d(S_8)/dt]_0 = k(S_8)_0^{0.6}$ which are listed in Column 3 of Table III.

For the interpretation of the above findings it is of great importance that a linear relationship exists between starting rate and starting concentration as shown in Figure 5. This confirms what other authors previously reported, namely, that a discrepancy exists between the time-law and the concentration dependence of the rate. This may be expressed as follows: in the reaction of sulfur with rubber, the sulfur decrease (at 150°) up to 25 mmoles per 100 g of compound follows the 0.6th order; however, the dependence of starting rate on

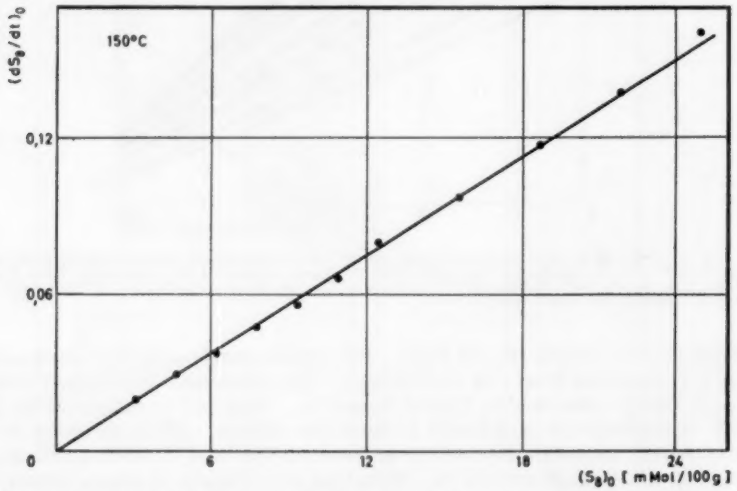

FIG. 5.—Dependence of sulfur decrease starting rate from the starting concentration in the region of complete sulfur solubility at 150° (reaction of NR with sulfur). Ordinate: $(dS_8/dt)_0$. Abscissa: $(S_8)_0$ [mmole/100 g.].

the sulfur starting concentration follows the 1st order law in agreement with van Rossem and Webster[8]. Therefore, we have the time law $d(S_8)/dt = k(S_8)^{0.6}$ and the concentration dependence $[d(S_8)/dt]_0 = k(S_8)_0$.

One finds now that a similar discrepancy found in accelerated vulcanization was of a somewhat different type; for generally the starting rate versus starting concentration did not give a straight line nor could this relationship be described by a simple exponent law; this was the cause for postulating a catalytic intermediate[1,2]. The discrepancy between time law and concentration dependence that has now also been confirmed in pure sulfur vulcanization, cannot be neglected without considering the effect of the reaction products on the sulfur decrease; it should be correct to assume with van Iterson[3] that the fractional reaction order is due to autocatalysis, namely, catalysis by reaction products[11]. All the more one must consider the fact that a first order reaction was found with respect to the sulfur concentration (Figure 5). Inquiring as to the reason why the starting rate of sulfur decrease is a linear function of the starting sulfur

concentration, one can assume with Gordon[12] that the rate determining step for the sulfur decrease is the spontaneous thermal opening of the S_8 ring. If this is the case, the basis for the relationship pictured in Figure 5 should be a unimolecular reaction. One must also remember that a 1st order concentration dependence could also be found if the structural units of gum rubber are directly involved in the cleavage of the S_8 ring—as they most always are. While this would be a bimolecular reaction, one would observe a 1st order sulfur decrease (pseudo-monomolecular) because of the presence of a large excess of gum rubber. What actually happens cannot be decided on basis of the kinetic results given here. Should it be possible to show that synthetic rubber reacts with sulfur at the same rate as natural rubber, the idea of Gordon would be well supported; investigation of model compounds (cyclohexene, dihydromyrcene, geraniol, etc.) should be more informative since the relationships could be studied under conditions of commensurate concentrations of the reactants. Such investigations are being conducted at the laboratories of the British Rubber Producers' Research Association, Welwyn Garden City[13].

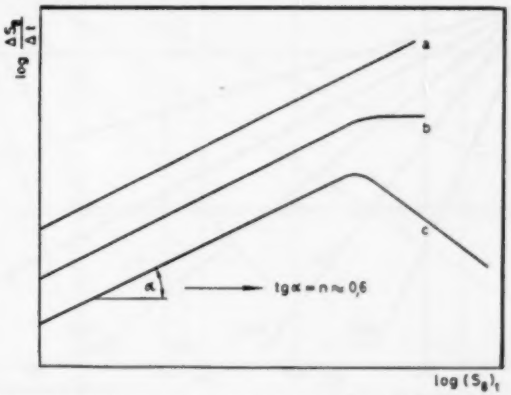

FIG. 6.—Schematic, log/log presentation of the relation between the rate of sulfur decrease and the concentration (reaction of NR gum with sulfur). Ordinate: log $\Delta S_8/\Delta t$. Abscissa: log $(S_8)_t$.

It should now be pointed out that the straight lines in Figure 4 for $t = 0$ and $1/1–0.6(S_8)_0^{1-0.6}$ do not terminate in the ordinate. Lines drawn perpendicular to the ordinate at those values intersect the straight lines at finite vulcanization time; this gives the impression that pure sulfur vulcanization has an induction period. We would rather not draw this conclusion but rather assume that this is due to a peculiarity of the kinetics of the sulfur decrease which could only be well defined at much higher sulfur concentrations. This leads us to a discussion of the conditions found at the concentration range of 25 to 75 mmoles S_8 per 100 g of compound as depicted by the curves in Figure 3b. One should notice that the convex curves of Figure 3a become concave at higher sulfur concentration (3b). The concentration at which this becomes noticeable in each case would depend obviously on the temperature. In the present case (150°) this peculiar curvature becomes increasingly noticeable above S_8 = 25 mmoles in 100 g compound; in particular these curves show a more clearly defined point of inflection at higher concentrations. The cause for the shape of these curves may lie in the fact that above 25 mmoles S_8 the region of in-

complete solubility of sulfur in rubber is reached; and if autocatalysis does not complicate the situation, one should find zero order portions of the curves; the length of these portions should increase at higher sulfur starting concentrations. The autocatalysis suppresses this effect considerably and imparts to the curves finally the concave shape. It seems, then that along portions of these curves, a sulfur decrease according to zero order takes place which is catalyzed by reaction products. After passing the point of inflection in the direction of longer reaction time, the sulfur decrease may again take place in a single phase (homogeneously). It can actually be shown that in this range the 0.6th order time law again holds. It is well known that one can determine the reaction order by using the equation $dc/dt = kc^n$ (c = concentration). By taking

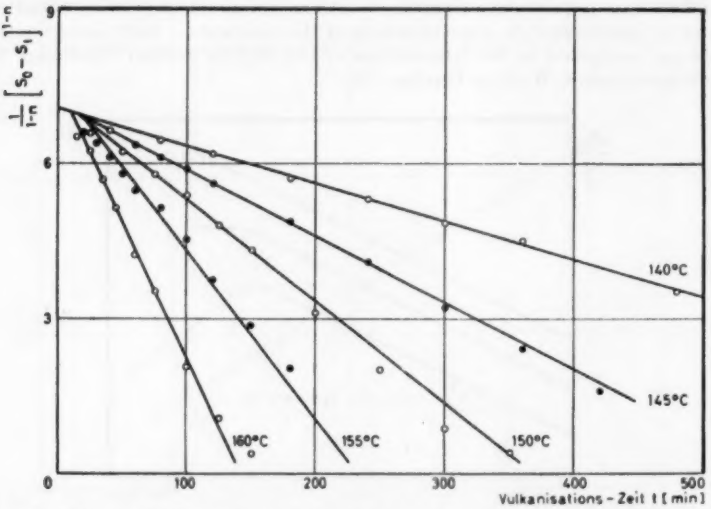

FIG. 7.—Reduction of sulfur concentration according to the 0.5th order in the reaction of NR gum with sulfur in the presence ZnO at different temperatures. 12.5 mmoles S_8 and 50 mmoles ZnO per 100 g of compound. Ordinate: $1/1-n\ (S_0-S_t)^{1-n}$. Abscissa: Vulcanization time t (min.).

logarithms and replacing partial differentials, the following is obtained: $\log \Delta c/\Delta t = \log k + n \log c$, by plotting $\Delta c/\Delta t$ against the concentration on log/log paper, a straight line should be obtained whose slope should be equal to the reaction order n. When data of Figure 3a and 3b were analyzed in the above fashion, graphs of Figure 6 are obtained, which clarify the above discussion. When studying these curves one should remember that by following the abscissa to the right, one moves toward the region of the start of the reaction. Three typical curves are obtained that resemble the three conversion curves developed by Lewis, Squires, and Nutting[14]. At 150°, the temperature used in our experiments, curve "a" is observed up to about 25 mmoles S_8 per 100 g of compound and it indicates that the 0.6th order is followed throughout the reaction. It corresponds to the curves in Figure 3a. With intermediate concentrations one can obtain curves of type b, that show short regions of constant rate at the start of the reaction (right side of the graph), the remainder again following the 0.6th order. These are curves that cover the transition between complete and

partial solubility of sulfur. Type *c* is found with very high sulfur concentrations and correspond to the curves in Figure 3b. We find a "negative" reaction order in the beginning of the reaction, while toward the end of the reaction (toward the left of the maximum) the slope again approaches $n = 0.6$, corresponding to the convex portion of the curves in Figure 3b.

In the face of these experimental results one wonders why some experimenters[7] came to the conclusion that the sulfur decrease was a zero order process. It is almost impossible to evaluate this on hand of the survey made by Springer[6]. It should be mentioned that it is easy to come to this conclusion when experimenting in the concentration range where complete solubility of sulfur borders on partial solubility. An inspection of the curves for 18.75 and 25 mmoles S_8 in Figure 3a, respectively 3b make this clear. Otherwise, it

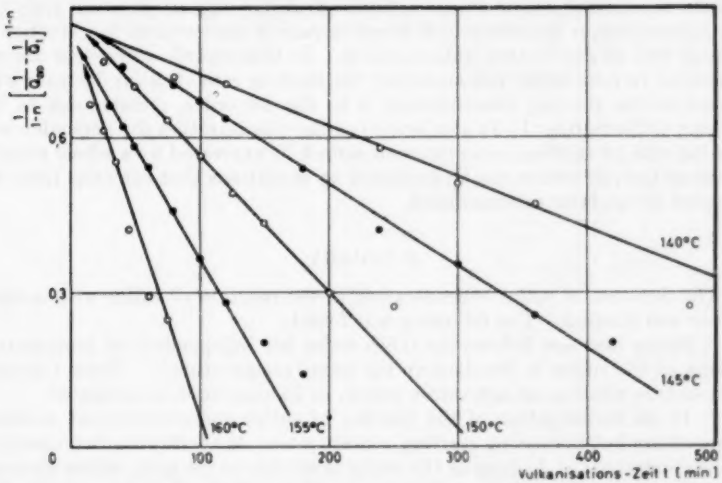

FIG. 8.—Course of the reciprocal equilibrium swelling in benzene according to the 0.5th order in pure sulfur vulcanization in the presence of ZnO at different temperatures. 12.5 mmoles S_8 and 50 mmoles of ZnO in 100 g compound. Ordinate: $1/1 - n\left(\frac{1}{Q_8} - \frac{1}{Q_t}\right)^{1-n}$. Abscissa: Vulcanization time t (min.).

should be pointed out that at times it is difficult to determine the reaction order. It is always well to have a whole set of curves available and to measure conversion where possible over the complete range. Now it should be pointed out that basically the same results are obtained when the pure sulfur vulcanization is investigated in the presence of zinc oxide. This does not inhibit autocatalysis as we had previously assumed[15], for Figure 7 shows that here, too, sulfur decrease is still of fractional order at all temperatures. However, in this case one obtains the best straight lines by substituting $n = 0.5$ for the reaction order. The rate may furthermore be slightly accelerated by the zinc oxide, but the activation energy remains the same. It is remarkable that the crosslinking reaction as measured by equilibrium swelling is of the 0.5th order in the presence of zinc oxide, shown clearly by the straight lines in Figure 8. That would lead one to conclude that crosslinking is directly connected with the sulfur concentration decrease. In these experiments 12.5 mmoles S_8 and 50 mmoles zinc

oxide were used per 100 g of compound. Comparing finally kinetics of sulfur decrease in pure and accelerated vulcanization, the following may be stated according to our experience presented up to now: 1) In pure sulfur vulcanization, the rate of sulfur decrease, with respect to time, is of fractional order ($n = 0.6$), as long as the sulfur is completely dissolved in the gum rubber. In accelerated vulcanization, the rate of sulfur decrease against time is also of fractional order ($n = 0.7 \cdots 0.8$) through a wider concentration range of sulfur as well as accelerator. This seems to be the case for natural rubber as well as synthetic. 2) This fractional order with respect to reaction time may be caused by autocatalysis, exclusively in the case of pure sulfur vulcanization and partially in the case of accelerated vulcanization; this autocatalysis is effected by reaction products, possibly polysulfide crosslinks. 3) The activation energy of sulfur decrease is a) 35 kcal/mole in pure sulfur vulcanization and b) $28 \cdots 30$ kcal/mole in accelerated sulfur vulcanization. 4) A discrepancy between time law and concentration dependence of reaction rate is observed in the kinetics of pure as well as accelerated vulcanization. In this regard, differences are observed; a) In pure sulfur vulcanization, the starting rate of sulfur decrease with respect to the starting concentration is to the 1st order, possible due to the opening of the S_8 ring; b) In accelerated sulfur vulcanization the dependence of starting rate on starting concentration cannot be expressed by a whole number exponent law; its course can be explained by conditions that can arise from the presence of catalytic intermediates.

SUMMARY

The decrease of sulfur concentration in the reaction of sulfur with natural rubber was studied. The following was found:

1. Sulfur decrease follows the 0.6th order law independent of temperature as long as the sulfur is dissolved in the gum (temperature!). From the rate-temperature relation, an activation energy of 35 kcal/mole is calculated.

2. In an investigation of the kinetics of sulfur concentration at constant temperature but increasing starting concentration, the following two cases can be differentiated: a) As long as the sulfur is soluble in the gum, sulfur decrease still follows the 0.6th order, possibly due to autocatalysis; the linear relationship between starting rate and starting concentration shows that the process is 1st order with respect to the concentration; this may be the consequence of a thermal, rate determining cleavage of the S_8 ring. b) As the sulfur at higher concentration is only incompletely soluble in the gum, conversion curves with points of inflection are found; this becomes more pronounced at higher concentration. At the start of the reaction one finds an autocatalytic sulfur decrease basically of zero order; in the latter part of the reaction after passing the point of inflection a 0.6th order is observed, as in the range of complete sulfur solubility.

3. A discrepancy between the time law and the concentration-rate relationship is found in pure as well as accelerated sulfur vulcanization; these conditions are compared and discussed.

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RADICAL AND IONIC REACTIONS OF TETRAETHYLTHIURAM DISULFIDE *

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An investigation of the reactions of tetraethylthiuram disulfide (TETD) possesses a significant theoretical interest and has no small practical value inasmuch as this thiuram takes a part in the processes of vulcanization and degradation of rubber[1, 2]. According to the vulcanization theories of Farmer and Bloomfield[1, 3], sulfur reacts with α-methylenic hydrogen atoms to form polysulfide bonds. The thiuram compound activates this process in an as-yet unknown manner. It is known that TETD appears to be an active degradative agent for Thiokol type rubber, cleaving its chains at the sites of the sulfide bonds. The occurrence of degradation through the influence of thiurams is also known in other types of polymers which contain in their linear chains a numerically insignificant number of polysulfide links, e.g., polychloroprene.

In order to understand the mechanism of these reactions it is necessary first to investigate some of the properties of a thiuram such as TETD, reactions of radical dissociation, interaction with alkalies, and the character of the compounds formed. The pertinent literature[4] is rather scanty.

The radical dissociation of thiuram.—The literature contains no experimental proof of the radical dissociation of thiuram disulfides though Koch[5] has stated the possibility of such a process on the basis that a solution of a thiuram disulfide, on heating attains a color which fades out on cooling. The use of TETD in the role of initiator in the bulk polymerization of chloroprene[6] appears to afford indirect evidence of such dissociation; the products of a radical dissociation, however, have never been isolated.

The radical decomposition of TETD was investigated in a CCl_4 medium, in the absence of an initiator, at 145° C. We isolated a material $(C_2H_5)_2N—CS—SCl$ in a 46% yield, which could only result from the interaction of the radical $(C_2H_5)_2N—CS—S\cdot$ with CCl_4.

Further to this, in the reaction products was some CS_2 and a material which analyzed as $(C_2H_5)_2NCl$, with a saponifiable chlorine atom. The formation of CS_2 and the latter compound, obviously, appears to be the result of two reactions between thiuram radicals and CCl_4:

$$(C_2H_5)_2N—\overset{\overset{S}{\|}}{C}—S\cdot \longrightarrow (C_2H_5)_2N\cdot + CS_2$$

$$\downarrow + CCl_4$$

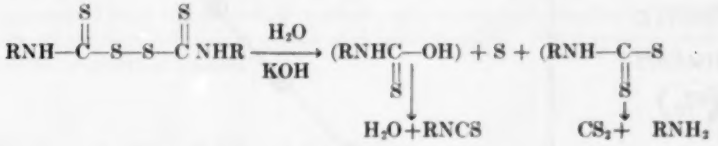
$$(C_2H_5)_2NCl + \cdot CCl_3$$

In this manner, through radical dissociation of thiuram, occur the following products of decomposition:

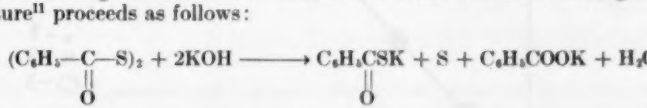
$$(C_2H_5)_2N—\overset{\overset{S}{\|}}{C}—SCl\ (46\%);\ (C_2H_5)_2NCl\ (44\%);\ CS_2\ (43\%).$$

* Translated by J. R. Robinson from *Zhurnal Obshchei Khimii SSSR*, Vol. 30, pages 794–798 (1960).

Ionic reactions of thiurams.—Tetramethyl- and tetraethylthiuram disulfides react with potassium cyanide in aqueous alcoholic solution, losing one atom of sulfur to form the thiuram monosulfides[7]. Upon this property of the thiuram disulfides is based, by some authors, the explanation of its use as a vulcanizing agent[8, 9]. The literature provides data on the decomposition of the dialkylthiuram disulfides in aqueous alkali[10]:

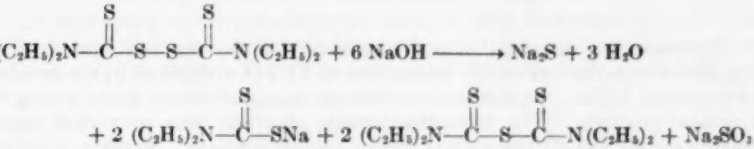


In an analogous manner the reaction of those disulfides having a similar structure[11] proceeds as follows:



In the case of the tetrasubstituted thiuram disulfides, data on their interaction with alkali is lacking in the literature. We have shown that this reaction proceeds by a mechanism different from that of the dialkyl compounds which have labile hydrogen atoms on the nitrogen and have in consequence greater reactivity and less thermal stability than the tetrasubstituted derivatives.

We looked into the reaction of TETD with NaOH and NH_4OH. Based upon our findings we can set up this reaction scheme:



Ammonia reactions proceed similarly, the only difference being a lower velocity of reaction, corresponding to its more feeble basicity. (see Table I). As seen in the data of the table, the ratio of diethyldithiocarbamate to thiuram monosulfide is 1:2 in all experiments, which corresponds to a reduction of the former compound in the reaction equation.

TABLE I

INTERACTION OF TETRAETHYLTHIURAM DISULFIDE WITH BASES

Base used	Base conc., %	Reaction time hr	Products of reaction, yield based on starting thiuram			
			Unreacted	Monosulfide	Diethyl dithiocarbamate	Split out sulfur
NaOH aq	2.0	8	—	58.0	31.0	98.0
NaOH alc	2.0	6	31.0	40.0	22.0	93.0
NH_4OH aq	2.0	8	45.0	32.0	15.2	92.0
NH_4OH alc	2.0	6	65.0	17.0	10.0	89.0

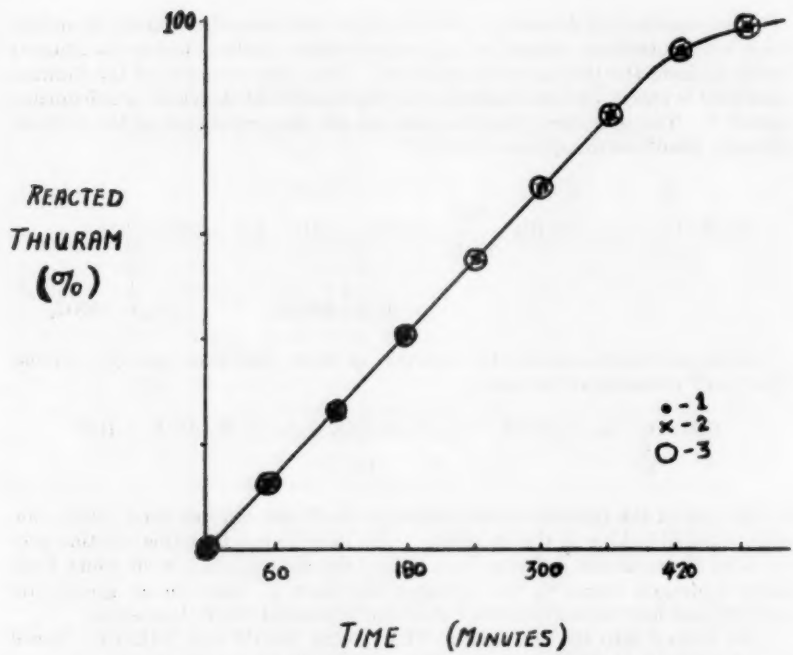


FIG. 1.—The influence of initiator ($K_2S_2O_8$) and inhibitor (PBNA) on the rate of reaction of TETD with alkali. *1*, without initiator; *2*, 3% $K_2S_2O_8$; 3, 2% PBNA.

To assess the accuracy of our suggestion for the reaction equations, we conducted experiments on the interaction of TETD with alkali in the presence of elemental sulfur. In this case, no thiuram monosulfide was found among the reaction products. The tetraethylthiuram disulfide was converted almost quantitatively (95.4%) to sodium diethyldithiocarbamate. Further, Na_2S and Na_2SO_3 were formed, quantitatively according to the equation:

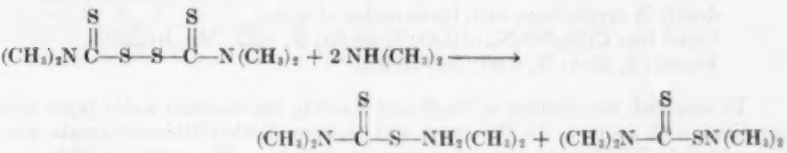
$$(C_2H_5)_2N{-}\overset{\overset{S}{\|}}{C}{-}S{-}S{-}\overset{\overset{S}{\|}}{C}{-}N(C_2H_5)_2 + 2S + 6\ NaOH \longrightarrow$$

$$2(C_2H_5)_2N{-}\overset{\overset{S}{\|}}{C}{-}SNa + 3H_2O + Na_2S + Na_2SO_3$$

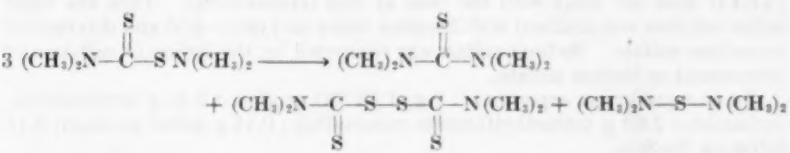
The absence of any thiuram monosulfide from the reaction products indicates that its formation is tied in with the splitting out of sulfur.

In confirmation of the ionic character of the reaction of thiuram with base, we studied the kinetics of this reaction in the presence of an initiator of potassium persulfate, and an inhibitor, phenyl-2-naphthylamine (PBNA). As is obvious from Figure 1, neither the inhibitor nor the initiator have an influence upon the rate of this reaction, which gives a sound basis for stating that the reaction of TETD with base is ionic in character.

The interaction of tetraethylthiuram disulfide with diethylamine.—Analogously to the studies with other bases, we also studied the reaction of tetraethylthiuram disulfide with diethylamine. This reaction has been studied by several investigators[12–14]. Delepine[12] reported that this reaction (in the case of the methyl homologs) produced dimethylammonium dimethyl dithiocarbamate, sulfur and tetramethylthiourea. Bedford and Gray[13], reported, instead of the thiourea, carbon disulfide. Craig and Davidson[14] carried out their reaction at 50° (as distinguished from the preceding workers, who made their studies at 100°) and in the presence of a five-fold excess of dimethylamine. They surmise that the reaction proceeds as follows:



The second product, on vacuum distillation, resulted in the formation of tetramethylthiuram disulfide, tetramethylthiourea, and tetramethyldiaminosulfide:



On interaction of tetraethylthiuram disulfide with diethylamine at 60°, we isolated diethylammonium diethyl dithiocarbamate, conforming to the equation of Craig and Davidson. The other reaction products were not examined.

EXPERIMENTAL

Radical dissociation of TETD.—Three g (0.01 mole) of TETD was heated with 30 g (0.2 mole) of carbon tetrachloride in a sealed-flask (ampule) in a nitrogen atmosphere. After heating 8 hours at 145–150°, the products isolated were:

1. 1.68 g. of material, crystallized from benzene—m.p. 46–46.5°.
   Found: % S, 34.9; Cl (total) 19.47; Cl (saponifiable) 19.5; N, 7.82 Mol. wt. 187.3 for $C_5H_{10}NS_2Cl$ calcd: S, 34.88; Cl (total) 19.3; Cl (saponifiable) 19.3; N, 7.75%; Mol. wt. 183.5.
2. 0.92 g. of crystalline material, insol. in most organic solvents; deliquescent in air; not fusible; on heating to 170–180° it darkens and chars.
   Calcd for $(C_2H_5)_2NCl$; N, 13.0; Cl, 32.98%.
   Found: N, 12.89; Cl, 33.04%.
3. 0.66 g. of CS_2 which was characterized as follows: after opening the ampule, the residual CCl_4 solution was treated with alcoholic base, the excess base neutralized, and the resulting xanthogenate was titrated with iodine.

Interaction of TETD with bases.—Five g (0.017 mole) of TETD in benzene solution was heated for 8 hours with stirring with aqueous (or alcoholic) solution of NaOH (70 g 2% solution = 0.034 mole). The products found were:

1. 2.6 g (58% of the initial thiuram) as tetraethylthiuram monosulfide. On recrystallization, m.p. = 64–65°.
   Calcd for: $C_{10}H_{20}N_2S_3$: S, 36.36; N, 10.38%; Mol. wt.: 264.0.
   Found: S, 36.36; N, 10.2%; Mol. wt.: 259.0.
2. 2.35 g. sodium diethyldithiocarbamate (separated by concentration of the water layer); 31% of the initial thiuram. After recrystallization from water-alcohol, m.p. 94–96°. Literature[b] cites m.p. 92–102°; evidently it crystallizes with three moles of water.
   Calcd for: $C_5H_{10}NS_2Na \cdot 3H_2O$: S, 28.55; N, 6.22; Na, 10.22%.
   Found: S, 28.4; N, 6.05; Na, 10.0%.

To establish the content of Na_2S and Na_2SO_3, the residual water layer was oxidized with iodine. In this way, any sodium diethyldithiocarbamate was converted to TETD and separated as a precipitate. The sodium sulfide was changed by the iodine to sodium iodide and elemental sulfur, which came down mixed with the thiuram. The precipitate of TETD and sulfur was treated with 10% aqueous base in the cold. The sulfur was dissolved by the alkali (TETD does not react with the base at this temperature). Then the basic sulfur solution was oxidized with bromine water and nitric acid and determined as sodium sulfate. Sodium sulfite was converted by the iodine to sulfate and determined as barium sulfate.

In an equilibrium experiment: 5 g of TETD produced 2.35 g diethyldithiocarbamate; 2.60 g tetraethylthiuram monosulfide; 0.16 g sulfur as Na_2S; 0.17 sulfur as Na_2SO_3.

Reaction of TETD with base in the presence of elemented sulfur.—10 g (0.0338 mole) TETD was heated in benzene solution (100 g of benzene) with 2.2 g. (0.07 mole) or elemental sulfur and 165 g of a 5% solution of NaOH (0.2 mole). The product was 14.5 g (94.4%) of sodium diethyldithiocarbamate.

Calcd for $C_5H_{10}NS_2Na \cdot 3H_2O$:S, 28.55; N, 6.22%.

Found: Total sulfur as Na_2S, 0.98 g; Total sulfur as Na_2SO_3 0.95 g (43.8%) S, 28.7; N, 6.33%.

Reaction of TETD with diethylamine.—Five g (0.017 mole) of TETD was heated to a temperature of 60° for 8 hours with 2.46 g (0.034 mole) of diethylamine dissolved in 20 ml of water. After separation of the layers, and evaporation of the water phase, 3.2 g of material remained; recystallized, its m.p. was 48–49°. On oxidation with iodine, a quantitative conversion to TETD was obtained.

SUMMARY

1. Investigation of the process of radical dissociation of TETD in carbon tetrachloride indicates that at 145° thiuram radicals are formed which react with the carbon tetrachloride to form $(C_2H_5)_2N—\underset{\underset{S}{\|}}{C}—SCl$ and CS_2.

2. A quantitative determination of the products of the base-influenced dissociation of TETD was carried out. A kinetic investigation of this reaction, in which initiator ($K_2S_2O_3$) and inhibitor (PBNA) were shown to have no velocity effect whatever, indicates that the process is an ionic one.

3. It is shown that in the reaction of TETD with diethylamine, one of the reaction products appears to be diethylammonium diethyldithiocarbamate.

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REVERSION DURING TMTD VULCANIZATION *

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The formation of a technically useful tetramethylthiuram disulfide (TMTD) cured rubber is largely determined by the type of metal oxide or salt in the mixture. We explain this function of metal oxides or salts by means of secondary reactions which tie up the product of interaction of a thiuram disulfide with rubber—a dialkyldithiocarbamic acid[1]. This process has considerable influence on the quality of the resulting vulcanizates. In the presence of zinc oxide or zinc salts, the dithiocarbamic acid is combined in the form of the zinc dithiocarbamate. In the absence of metal oxides and in mixtures with magnesium and calcium oxides or salts the dithiocarbamic acid decomposes into a dialkylamine and carbon disulfide (with calcium oxide some binding occurs). TMTD prepared vulcanizates containing zinc oxide are characterized by the best mechanical properties and in this case reversion is absent—the number of crosslinks is not diminished by prolonged heating under vulcanization conditions.

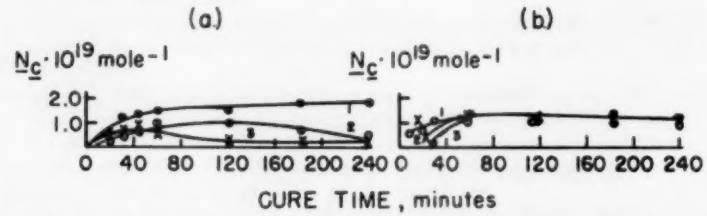

Fig. 1.—Variation of the crosslink density (N_c) during vulcanization at 143° in a press of a mixture of SKI and TMTD, preparation: *a*—in air; *b*—in argon. Composition of the mixtures in parts by weight: *1*) SKI 100, TMTD 3, zinc oxide 5; *2*) SKI 100, TMTD 3, magnesium oxide 2.5; *3*) SKI 100; TMTD 3.

Significantly poorer mechanical properties and a pronounced reduction of the crosslink density of the vulcanizates is observed after attainment of a certain maximum during vulcanization with TMTD in a press if the mixture contains no metal oxides or contains magnesium or calcium oxides or their salts (Figure 1a). In these cases decomposition of dithiocarbamic acid takes place with the evolution of carbon disulfide and dimethylamine. Consequently, it was conjectured that the cause of reversion ought to be sought in the action of these volatile products because according to the amount of combined sulfur and nitrogen of TMTD all of the vulcanizates are essentially the same.

It was of interest to investigate the influence of oxygen on TMTD vulcanization. With this in mind mixtures were prepared from synthetic isoprene rubber (SKI) with TMTD on a micromill enclosed in an inert atmosphere (argon). The mixtures were sealed in a cellophane package in argon and were

* Translated by Earl C. Gregg, Jr. for Rubber Chemistry and Technology, from Vysokomolekulyarnya Soedineniya **2**, 514–517 (1960).

vulcanized in a press at 143°. As seen in Figure 1b, upon curing these mixtures reversion (optimum vulcanization) is not observed. The crosslink density is practically the same for all of the indicated vulcanizates but in air is at a lower level during vulcanization without metal oxides and with magnesium oxide.

To judge from the amount of combined and total sulfur from TMTD in the vulcanizates the interaction of TMTD with rubber in an argon atmosphere occurs in the same way as it does in air (Figure 2).

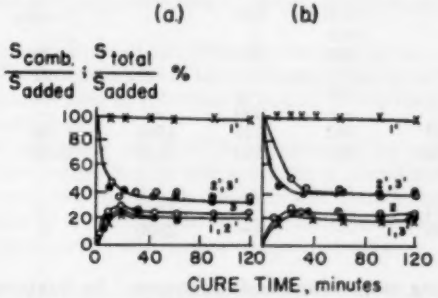

FIG. 2.—Kinetics of combined sulfur (1, 2, 3) and variation of total sulfur of TMTD (1′, 2′, 3′) in process of vulcanization of a mixture of SKI and TMTD in a press at 143°: *a)* mixutre prepared in air; *b)* mixture prepared in argon. Designations the same as in Figure 1.

The amount of dimethylamine and carbon disulfide obtained from mixtures without oxides and from mixtures containing magnesium oxide both prepared in argon is the same as from mixtures prepared in air. In mixtures containing zinc oxide volatile components are not formed.

All the facts indicate that reversion in mixtures containing thiuram may be explained by the presence of molecular oxygen and active oxygen containing compounds even in those small amounts which remain under the conditions of vulcanization in a press. Oxygen and oxygen containing compounds cause

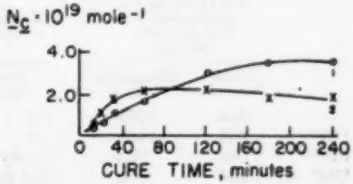

FIG. 3.—Variation of the network density, N_c, in vulcanization of mixtures from NR and TMTD in a press at 143°. Composition of the mixture in parts by weight: *1)* NR 100, TMTD 3, zinc oxide 5, PBNA 1; *2)* NR 100, TMTD 3, zinc oxide 5.

degradation of the vulcanizate network by destructive oxidative processes which are intensified by dimethylamine and carbon disulfide formed by decomposition of dimethyldithiocarbamic acid in mixtures without zinc oxide. Conversely, zinc dimethyldithiocarbamate prevents the oxidative degradation of the vulcanizate and therefore reversion does not appear during vulcanization of mixtures of natural rubber (NR) and SKI with TMTD even though prepared in air.

The most effective formation of crosslinks results if an ordinary antioxidant such as PBNA is present (Figure 3). With a rise in temperature reversion in

TABLE I

VARIATION OF THE EQUILIBRIUM SWELLING OF VULCANIZATES FROM NR TMTD AND ZINC OXIDE OR MAGNESIUM OXIDE AT VARIOUS TEMPERATURES. (MIXTURES PREPARED IN AIR.)

Cure time, min.	Equilibrium Swelling, %: Mixture: NR 100, TMTD 3, zinc oxide 5, PBNA 1			Mixture: NR 100, TMTD 3, magnesium oxide 2.5, PBNA-1		
	120°	143°	160°	120°	143°	160°
10	—	1400	542	—	Soluble	1645
20	—	1350	—	—	gel	—
30	—	908	535	—	6500	4140
45	—	—	—	—	2040	5400
60	—	750	—	—	1190	—
80	—	—	600	—	—	7350
120	902	552	520	1585	1109	7530
240	672	501	560	1525	2010	Highly swollen gel
480	603	—	—	1945	—	—
840	628	—	—	2800	—	—

mixtures containing magnesium oxide increases. In mixtures with zinc oxide reversion does not manifest itself up to a temperature of 160°. The limiting network density in the presence of zinc oxide is nearly independent of the vulcanization temperature (cf. Table I).

According the reasons referred to above the resistance to thermal aging of vulcanizates of SKI with TMTD and zinc oxide is considerably greater than with magnesium oxide (Table II).

TABLE II

VARIATION OF OPTIMUM PHYSICAL PROPERTIES OF THIURAM VULCANIZATES AFTER AGING. (MIXTURE PREPARED IN AIR AND VULCANIZED IN A PRESS AT 143°.)

Condition of test	Mix: SKI 100, TMTD 3, ZnO 5, stearic acid 1, PBNA1; cure, 60 min: Tensile Kg/cm²	Elongation %	SKI 100, TMTD 3, MgO 2.5, stearic acid 1, PBNA 1; cure, 45 min: Tensile Kg/cm²	Elongation %
Before Aging	240	1050	110	1540
After 20 hours aging at 110°	185	1100	38	800
After 6 hours aging at 150°	165	965	Sticky mass	
After 12 hours aging at 150°	104	860	The same	

The age resistance is drastically reduced if zinc dialkyldithiocarbamate is removed from the vulcanizates by extraction[2].

The influence of various dithiocarbamates on aging of vulcanizates according to the rate of stress relaxation at 100° C in air was examined by Dun and Scanlon[3]. Zinc dialkyldithiocarbamate effectively protects peroxide and thiuram vulcanizates from aging.

These authors think that zinc dithiocarbamate and several others decompose the peroxides and hydroperoxides formed during oxidation of rubber. This agrees with our point of view about the nature of reversion in thiuram vulcanizates.

CONCLUSIONS

1) Reduction of crosslink density of vulcanizates (reversion of vulcanization) is observed during vulcanization of a mixture prepared in air of NR and SKI with TMTD without metal oxides and with magnesium and calcium oxides. In these cases the dimethyldithiocarbamic acid formed during vulcanization decomposes into carbon disulfide and dimethylamine.

2) During mixing and curing of these mixtures in an argon atmosphere reversion is absent although evolution of carbon disulfide and dimethylamine is observed.

3) During vulcanization of the mixtures containing zinc oxide no reversion occurs as a result of preparation of the mixtures either in air or in argon. Dimethyldithiocarbamic acid in this case is bound in the form of the stable zinc dimethyldithiocarbamate.

4) Reversion of rubber by TMTD is explained by oxidative destructive processes which are intensified by the products of decomposition of dimethyldithiocarbamic acid, i.e., by carbon disulfide and dimethylamine, and are suppressed by reaction of it to form zinc dimethyldithiocarbamate which serves as an inhibitor of the oxidative destruction of the vulcanizate.

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RADIATION CROSSLINKING OF RUBBER. III. CHAIN FRACTURE *

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INTRODUCTION

Exposure of hydrocarbon polymer molecules to high energy radiation results either in a decrease in their molecular weight or else in an increase with the eventual formation of an insoluble network. The primary factor determining the behavior is the relative incidence of fracture of the main chain of carbon atoms to crosslink formation. The ratio of fractures to crosslinks β has usually been estimated from studies of the solubility of irradiated polymers[1]. Most of this work has been on polyethylenes, but even under comparable experimental conditions widely differing estimates of β have been reported[2]. The use of stress-relaxation measurements to detect the fracture of network chains during irradiation has also been reported[3–5].

A recent study of the elastic behavior of crosslinked networks has indicated that comparative estimates of the number-average molecular weights of both (*1*) the chain segments lying between adjacent crosslinks and (*2*) the molecular chains crosslinked into the network may be obtained from stress-strain measurements alone[6–9].

In the present work an attempt has been made to apply all three methods in a study of chain fracture occurring during the irradiation of purified natural rubber *in vacuo*.

EXPERIMENTAL METHODS

MATERIALS

The natural rubber was lightly masticated in air and extracted with acetone in the dark for 24 hours at ca. 70° C. It was then dried and stored *in vacuo* and found to contain 0.3% of oxygen and 0.2% of nitrogen.

The de-proteinized natural rubber was not masticated but was similarly purified and was then found to contain 0.13% oxygen, 0.03% nitrogen, and 30% gel.

Stress-relaxation measurements were carried out on strips of rubber initially crosslinked by heating with dicumyl peroxide. These strips were similarly extracted and dried.

Number-average molecular weights were obtained on samples of each of the rubbers before crosslinking. These were determined from osmotic pressure measurements on solutions of the rubber in toluene using a Zimm-Meyerson osmometer with ultracellafilter *aller feinst* grade membranes. Measurements were made at 25 + 0.005° C at four concentrations of rubber and their value at zero concentration extrapolated from the resulting linear plots.

* Reprinted from the *Journal of Polymer Science*, Vol. 43, pages 35–47 (1960).

PREPARATION AND IRRADIATION OF SAMPLES

The rubber was warmed and pressed into sheets between glazed cloth. The sheets, still supported by the cloth, were thoroughly degassed and sealed in glass tubes at a pressure of ca. 10^{-5} mm Hg. The samples were then exposed to the electron beam from a 4-M.e.v. linear accelerator at a nominal dose rate of 5 Mrad per minute. During exposure the glass tubes were cooled in a blast of cold air.

DETERMINATION OF THE SOLUBLE FRACTION

Samples of irradiated rubber were cut up or pulverized into very small pieces and weighed in a small packet of lens tissue paper. The packet was then immersed in a very large volume of analytical grade benzene or toluene and the container thoroughly flushed with nitrogen before sealing. Preliminary experiments had shown that all the soluble rubber was extracted in 10 days, and this was the minimum period of immersion used in these experiments. On removal from the solvent the packets were dried *in vacuo* and the soluble fraction of the rubber estimated from the loss in weight after a very small correction had been made for the change in weight of the packet itself.

The use of a packet in this manner had been reported by Charlesby and Pinner[2] in the study of the solubility of irradiated polyethylene and is particularly suitable for the estimation of very small soluble fractions as it allows a large surface area of polymer to be in contact with the solvent and at the same time avoids the danger of small losses of gel.

MEASUREMENTS OF STRESS RELAXATION

Measurements were made with relaxometers described by Berry[10]. These were designed to reduce changes in strain during relaxation to a minimum. They were enclosed in glass jackets which enabled measurements to be made with the sample in a vacuum. The relaxometers were enclosed at a pressure of ca. 10^{-5} mm Hg, but it appeared that after transporting them to and from the electron accelerator some leakage had occurred; this was not measured, as hydrogen is evolved from the rubber during irradiation. The leakage was overcome in later experiments by replacing the high vacuum grease by a lithium stearate composition which permitted easier adjustment of the relaxometer key[11]. This grease had excellent resistance to heat and enabled the rubber strips in the relaxometers to be heated at 140° C for 24 hours *in vacuo* before irradiation. Moore and Scanlan[12] studying the stress relaxation of rubbers during further vulcanization with di-*tert*-butyl peroxide have shown that prior heating in this way considerably reduced a large degree of relaxation which occurred during early stages of stress relaxation and before a constant rate of relaxation was attained.

During irradiation which was carried out at 2.4 Mrad per minute the glass jackets were cooled in a blast of cold air. In some experiments irradiation was interrupted and the equilibrium stress measured ten minutes later.

The degrees of crosslinking before and after irradiation were calculated from equilibrium swelling measurements in *n*-decane at 25° C using a previously established relation between the equilibrium volume swelling and crosslink density[8]. No allowance was made for the possible different effect of crosslinks formed in the extended rubber strips ($\lambda \simeq 2$) on the equilibrium volume swelling.

STRESS–STRAIN MEASUREMENTS

The method used for the measurement of equilibrium stress-strain properties has been described previously[6]. Strips of rubber about 6 cm long and 0.5 cm wide were cut from sheets of irradiated rubber and two reference marks were made approximately 4 cm apart. Load-deformation measurements were made at 25° C, the separation of the reference marks was measured by a cathetometer 3 minutes after each increment of load.

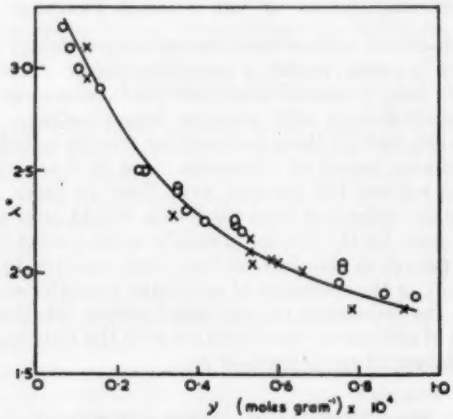

FIG. 1.—Empirical relation between λ^* and degree of crosslinking: (×) peroxide vulcanizates and (○) sulfur vulcanizates.

The results were analyzed by plotting $\frac{1}{2}fA_0^{-1}(\lambda - \lambda^{-2})^{-1}$ against λ^{-1}, where λ is the extension ratio produced by a load f in a sample with an original area of cross section A_0. At low and moderate extensions the behavior follows a linear relation given by the equation:

$$\tfrac{1}{2}fA_0^{-1}(\lambda - \lambda^{-2})^{-1} = C_1 + \lambda^{-1}C_2 \qquad (1)$$

At higher extensions departures from linearity occur and the value of $\frac{1}{2}fA_0(\lambda - \lambda^{-2})^{-1}$ increases rapidly with decrease in λ^{-1}. Values of C_1 and λ^*, the extension ratio at which the observed stress-strain curve departs from the linear portion by $2\frac{1}{2}\%$ of C_1, were obtained for each of the crosslinked rubbers and used to characterize their network structure.

Previous investigations[8,9] have shown that the values of C_1 reflect both the degree of crosslinking and the presence of network flaws due to chain ends and may be related to the degree of chemical crosslinks by the relation

$$C_1 = (\nu\rho RT + 0.78 \times 10^6)(1 - 1.15n\nu^{-1}) \text{ dynes cm}^{-2} \qquad (2)$$

where ν and n are the number of moles of chemical crosslinks and primary molecular chains, respectively, per gram of rubber. It was also shown[9] that the value of λ^* depended only on the degree of crosslinking and was independent of the initial molecular weight and an empirical relation describing the dependence of λ^* on degree of crosslinking was established and is shown in

Figure 1. These relationships obtained on rubbers vulcanized with di-*tert*-butyl peroxide and di-cumyl peroxide were derived with the explicit assumption that no significant degradation occurred during their vulcanization, and thus n was equal to n_0 the number of moles of primary molecular chains prior to vulcanization.

Estimates of the degree of crosslinking of each of the vulcanizates were determined from the values of C_1 and λ^*.

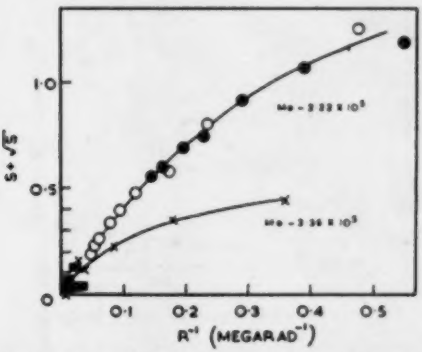

FIG. 2.—Relation between $S+S^{\frac{1}{2}}$ and the reciprocal of the dose (R): (○, ●, ×) acetone extracted rubber and (■) acetone extracted de-proteinized rubber.

EXPERIMENTAL RESULTS

SOLUBILITY MEASUREMENTS

The most refined analysis giving the partition of polymer molecules between sol and gel is that due to Charlesby and Pinner[2], which gives the following expression for sol fraction S, present after the irradiation of polymers with initially random distributions of molecular weights.

$$S + S^{\frac{1}{2}} = pq^{-1} + (qu_1R)^{-1} \tag{3}$$

where p and q are the fracture and crosslink densities, respectively, u_1 the number-average degree of polymerization, and R the radiation dose.

Results obtained in the present investigation are shown in Figure 2, this gives $S + S^{\frac{1}{2}}$ as ordinate and R^{-1} as abscissa. It will be seen that the linear relation given by eq. (3) does not adequately describe the results. Charlesby and Pinner obtained a linear relationship at sufficiently high irradiation doses for a number of polymers, and it thus appears that a random molecular weight distribution may not have been formed in the present work. Figure 2 also shows that the sol fraction rapidly approaches zero with increase in radiation dose and indicates that there is very little consummated random chain fracture. In view of the nature of the results, quantitative analysis in terms of p and q is not justified.

These conclusions are in general agreement with a previous result of Charlesby[12] who reported that the sol fraction of a natural rubber had decreased to less than 1% after a dose of several hundred Mrad in an atomic pile. From this he deduced that β was less than 0.1 although it must be noted that the low

figure for the sol fraction is puzzling as unpurified natural rubber contains several per cent soluble nonpolymeric material. Charlesby has also shown that estimates of β can be obtained from the shape of the curve obtained when the logarithm of S is plotted against the logarithm of R[14]. Data of this kind have been reported by Charlesby and Groves[15] for natural rubber but no estimate made of β presumably because of the marked divergence from a random molecular weight distribution.

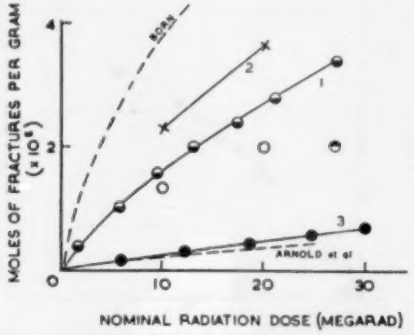

FIG. 3.—Dependence of number of fractures, determined from stress relaxation, on radiation dose: (×) λ =2.0 (10^{-3} mm); (◒) λ =2.1; (○) λ =2.0; (◒) λ =1.7; and (●) λ =1.6 (10^{-3} mm).

STRESS–RELAXATION MEASUREMENTS

It is generally assumed that the stress in a rubber vulcanizate maintained at constant elongation is decreased by fracture of network chains but is unaffected by additional crosslinking. With an additional assumption that each fracture in the effective network removes one chain, Tobolsky[16] has shown that the number of moles of fractures per gram of rubber q is given by

$$q = - N_0 \log f f_0^{-1} \tag{4}$$

where N_0 is the initial number of moles of elastically effective chains per gram of rubber and $f f_0^{-1}$ the ratio of stresses after and before relaxation.

Estimates of the value of N_0 have been obtained from stress-strain or volume swelling measurements, and Tobolsky has used the simple relation

$$f = N_0 \rho R T \, (\lambda - \lambda^{-2}) \tag{5}$$

where λ is the extension ratio. In this present investigation the results were first analyzed by obtaining the value of C_1 prior to irradiation from equilibrium volume swelling measurements and putting

$$C_1 = \tfrac{1}{2} N_0 \rho R T \tag{6}$$

Values of q were then determined from eq. (4).

The results are shown in Figure 3 which gives the estimated value of the number of fractures q as a function of period of irradiation. Curve 1 obtained in the earliest experiment was not reproducible, and it appeared that difficulties

in maintaining a hard vacuum were the source of this variability. Curve 2 shows results on samples irradiated in air at a pressure of 10^{-3} mm, and it is clear that small amounts of air have a marked effect in increasing the rate of relaxation. Curve 3 shows the results of the final experiment in which the usual high vacuum grease was replaced by a lithium stearate composition and in which the samples were heated *in vacuo* prior to irradiation. These modifications resulted in a much lower rate of chain fracture and, as reported by Moore and Scanlan, prior heating drastically reduced the large initial relaxation of stress. Figure 3 also includes an approximate representation of results reported by previous workers although in these cases differences due to the presence of compounding ingredients might be anticipated.

Mullins and Thomas[17] have recently shown that Tobolsky's assumption that each fracture in the network removes one chain only applies to the first few fractures in a network formed by crosslinking an infinitely long molecule, and that, for vulcanizates with network structures similar to those examined here, the use of eq. (4) overestimates the number of fractures by a factor of approximately two. Further, Moore and Watson[7] and Mullins[8] have shown that chain entanglements may make a significant contribution to the stress. Thus in the determination of N_0 an appropriate allowance should be made.

The experimental results have been further analyzed in an attempt to make allowance for these developments. In the first of these Mullins and Thomas' new theory describing the effect of fractures on elastic properties has been used and no attempt made to allow for entanglements. In the second an empirical expression derived by Mullins in a study of the elastic behavior of peroxide vulcanizates has been used; this introduces a correction for entanglements.

(*a*) *First analysis.*—An approximate representation of Mullins and Thomas' theory for vulcanizates with network structure similar to those examined here (viz., $n\nu^{-1} < 1$) is given by

$$N = 2\nu(1 - 0.55n\nu^{-1}) \tag{7}$$

where N is the number of elastically effective chains, ν the number of crosslinks, and n the number of primary chains. Alternatively this can be expressed as

$$C_1 = \nu\rho RT\ (1 - 0.55n\nu^{-1}) \tag{8}$$

It was assumed that crosslinks formed during stress relaxation made no contribution to the stress and that the stress was proportional to the number of chains which were present initially and which still remain effective. Then using eq. (8):

$$f \cdot f_0^{-1} = C_1 \cdot C_{10}^{-1} = (1 - 0.55n\nu_0^{-1})(1 - 0.55n_0\nu_0^{-1})^{-1} \tag{9}$$

where the subscript zero refers to the rubber before irradiation.

Values of n_0 and ν_0, before irradiation, and n and ν, after irradiation, were determined as follows. Measurements of equilibrium volume swelling before irradiation together with intrinsic viscosity measurements on similar samples of rubber before vulcanization permitted the determination of C_{10} and n_0, respectively, and from eq. (8) an estimate of ν_0 was obtained. Stress-relaxation measurements in conjunction with eq. (9) gave an estimate of n, and finally equilibrium volume swelling measurements after irradiation gave a value of ν.

TABLE I

STRESS RELAXATION MEASUREMENTS
Sample 3 (λ during irradiation: 1.6. Radiation dose: 30 Mrad)

	v_r[a]	C_1 (dynes × 10^{-6})	f/f_0	$n \times 10^4$	$\nu \times 10^4$	β
1st Analysis						
Before	0.265	1.28	1.000	4.0	0.59	—
After	0.323	2.10	0.904	13.8	1.01	0.18
2nd Analysis						
Before	0.265	1.28	1.000	4.0	0.32	—
After	0.323	2.10	0.904	5.0	0.63	0.03

[a] Here v_r is the volume fraction of rubber in the swollen material.

The number of chain fractures q and crosslinks p during irradiation was then given by $n - n_0$ and $\nu - \nu_0$, respectively.

(*b*) *Second analysis.*—The following empirical relation for C_1 was derived in a previous study of the behavior of peroxide vulcanizates[8]:

$$C_1 = (\nu\rho RT + \alpha)(1 - 1.15n\nu^{-1}) \tag{10}$$

where α is 0.78×10^6 dynes cm^{-2} and represents the contribution of entanglements to the retractive force and ν refers to chemical crosslinks only. In the

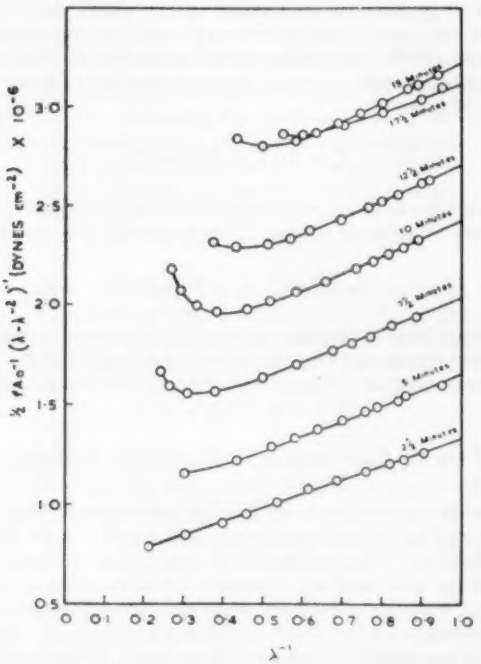

FIG. 4.—Relation between $\frac{1}{2}fA_0^{-1}(\lambda - \lambda^{-2})^{-1}$ and λ^{-1}.

TABLE II

NETWORK PARAMETERS FROM STRESS–STRAIN MEASUREMENTS
(Dose rate: 5 Mrad/min. $n_0 = 3.0 \times 10^{-6}$)

Period of irrad., min	C_1 (25° C) dynes $\times 10^{-6}$	C_2 (25° C) dynes $\times 10^{-6}$	λ^*
2½	0.63	0.69	—
5	0.88	0.80	2.70
7½	1.20	0.84	2.38
10	1.53	0.90	2.08
12½	1.78	0.93	1.98
15	2.23	1.00	1.88
17½	2.37	0.76	1.83
20	broke		

determination of this relationship it was assumed that no degradation of primary molecular chains occurred during the vulcanization of peroxide rubbers.

Adopting equivalent assumptions to those in the first analysis this gives

$$ff_0^{-1} = (1 - 1.15n\nu_0^{-1}(1 - 1.15n_0\nu_0^{-1})^{-1} \qquad (11)$$

Equations (10) and (11) were then used as in the first analysis to determine values of $n - n_0$ and $\nu - \nu_0$.

Table I gives the results of both analyses. The wide disparity of the two estimates for β reflect the need for further work to establish an adequate basis for the quantitative interpretation of stress-relaxation data. The very low value of 0.03 obtained when allowance is made for chain entanglements suggests that when crosslinking occurs at a higher rate than fracture, as in this investigation, entanglements which would be released by chain fracture alone may be locked into the network by the additional crosslinks.

STRESS–STRAIN MEASUREMENTS

Results of the stress-strain measurements obtained on samples subjected to different periods of irradiation are shown in Figure 4, and Table II gives values of C_1 and λ^* determined from these stress-strain curves together with the value of n_0 the number of primary molecular chains prior to vulcanization. Estimates of the degree of crosslinking ν obtained from the values of C_1 and λ^* are given in Table III.

The value of the degree of crosslinking determined from the measured value of C_1 is in all instances considerably less than that determined from λ^*. It appears that this is due to chain fracture as well as crosslinking occurring dur-

TABLE III

ESTIMATION OF THE DEGREE OF CROSSLINKING AND THE NUMBER OF PRIMARY MOLECULES (n)

Period of irrad., min	$\nu \times 10^4$ from C_1	$\nu \times 10^4$ from λ^*	$n \times 10^4$
0	—	—	0.03
2½	0.095	—	—
5	0.16	0.21	0.06
7½	0.28	0.35	0.07
10	0.41	0.50	0.08
12½	0.52	0.66	0.11
15	0.72	0.85	0.12
17½	0.79	0.93	0.14

ing irradiation. Under these circumstances the value of n_0 determined on the rubber prior to irradiation is not the value appropriate for the rubber after degradation during irradiation.

Values of λ^*, and hence estimates of the degree of crosslinking obtained from λ^*, have been shown to be unaffected by degradation of the primary molecular chains. Thus an estimate of chain fracture during irradiation can be readily obtained by determining the value of n in eq. (2) which results in identical values of the degree of crosslinking being obtained from C_1 to those obtained from λ^*.

Values of n calculated in this way are given in the last column in Table III.

The results are summarized in Figure 5. This shows the two estimates of the degree of crosslinking ν obtained from C_1 and λ^*, respectively, as a function of radiation dose. In addition the broken line shows the derived value of the extent of chain fracture $(n - n_0)$. The linear curves indicate that there is a

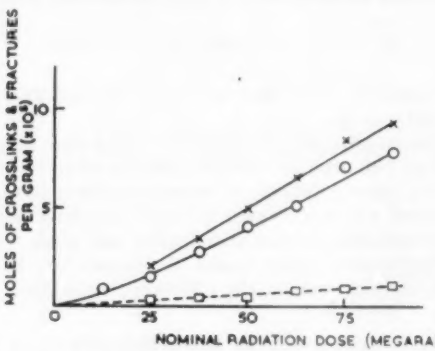

FIG. 5.—Dependence of number of fractures and crosslinks determined from stress-strain curves on radiation dose: (○) from C_1, (×) from λ^*, and (□) estimated fractures.

constant rate of chain fracture, and that after an initial retardation a constant rate of crosslinking. The value of β given by the ratio of these two rates is approximately 0.11.

DISCUSSION

Results from each of the three methods of estimating chain fracture and crosslinking during irradiation of natural rubber indicate that fracture resulting in two terminal chain ends is small. Quantitative estimates from solubility data were not attempted as the results did not follow theoretical predictions. Attempts to overcome inconsistencies in the analysis of stress-relaxation data provided two widely divergent values of β, and it is apparent that further development in the analysis of stress-relaxation data is necessary before reliance can be placed on their quantitative interpretation in terms of an absolute measure of chain fracture and crosslinks.

The analysis of stress-strain curves of rubbers crosslinked by irradiation gave a value of β of 0.11. This is based upon an empirical study of the effect of both the degree of crosslinking and the degree of breakdown of primary molecular chains on the stress-strain behavior of rubbers vulcanized by the thermal decomposition of di-*tert*-butyl peroxide. In this study it was assumed

that there was no further breakdown of the primary molecules during vulcanization, but recent work by Moore and Scanlan[12] suggests that there is fracture during the peroxide vulcanization of strained samples of natural rubber. No quantitative correction for this fracture is available, and the value of β of 0.11 will be an underestimate depending on the extent that fracture occurred in peroxide vulcanization.

Stress-strain measurements do not provide information on the possible recombination of fractured ends into the network to form trifunctional links. Charlesby[18,19] has suggested that this may be a frequent occurrence, and in this case the value of β determined from stress-strain measurements will again be an underestimate.

If it is assumed that bond fractures in polyisoprene due to irradiation occur randomly, then the ratio of fractures in the main chain to those in side groups will be 4 to 9. If further it is assumed that each side group fracture results in one crosslink[20] and if each main chain fracture results in two terminal chain ends, a value of β of approximately 0.44 is obtained.

The much lower value of β obtained in this investigation suggests that recombination of fractures in the main chain may be an important process and occur more readily than recombination of side group fractures.

The results shown in Figure 5 can be used to obtain an estimate of a $G(x)$ value. This is the number of crosslinks per 100 e.v. of energy absorbed and can be calculated from the relation

$$G(x) = 0.96n\,R^{-1} \times 10^5 \tag{12}$$

where n is the number of moles of crosslinks per gram of rubber and R the radiation dose in Mrad. The value of $G(x)$ of 0.96 for the highest dose is in reasonable agreement with a previously reported value of 0.75. If fractures are taken into account, the present value of $G(x)$ is increased to 1.05.

SYNOPSIS

Purified natural rubber has been exposed *in vacuo* to the 4-M.e.v. electron beam from a linear accelerator and attempts have been made to estimate the ratio of fractures of the main chain of carbon atoms to crosslinks, using three different methods. Measurements of the sol fraction (S) as a function of the radiation dose (R) did not conform to a linear relationship between $S + S^{\frac{1}{2}}$ and R^{-1} reported by Charlesby and Pinner for a number of other polymers. It appeared that in the present experiments there was little consummated random fracture, and it was found that the sol fraction tended toward zero at radiation doses above about 50 Mrad. The stress in rubbers maintained at constant elongation decreased continuously on irradiation, and it was found that rigorous exclusion of traces of air and impurities was of critical importance. Deficiencies of previous analyses of stress-relaxation data are disucsed and an attempt made to provide an internally consistent treatment of the data. In one treatment which made no allowance for the possible contribution of chain entanglements a value for β of 0.18 was obtained. In another treatment an attempt was made to allow for entanglements and a much lower value for β of 0.03 was obtained. This very low value may be due to the inadequacy of the assumption made that fracture inevitably releases entanglements under conditions where a much higher rate of concurrent crosslinking may serve to lock them into the network. Further work is required to establish a reliable basis for the

interpretation of stress-relaxation data. In a third method stress-strain measurements of irradiated rubber provided estimates of the number-average molecular weights of both (*1*) the chain segments between adjacent crosslinks and (*2*) the primary molecular chains. Comparison with similar data for vulcanizates prepared by thermal decomposition of di-*tert*-butyl peroxide gave a value for β of 0.11. This value was calculated on the assumption that no fracture occurs on formation of the peroxide vulcanizates and is, therefore, likely to be an underestimate. The nominal $G(X)$ value of 0.9 is increased to 1.05 when an allowance is made for fracture.

ACKNOWLEDGMENTS

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VULCANIZATION OF SBR IN A THERMAL NEUTRON FIELD *

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INTRODUCTION

Vulcanization of rubber by ionizing radiation has stimulated a great deal of active research in recent years[1–17]. However, there is a paucity of data concerned with vulcanization in a thermal neutron field. Induced radioactivity considerations have precluded the use of thermal neutrons. Davidson and Geib[3] found that the effects of pile radiation (gamma rays, fast neutrons, and thermal neutrons) could be promoted by the incorporation of generous amounts of ammonium borate into a rubber matrix. The boron gave rise to energetic, highly ionizing helium nuclei as a result of the following nuclear reaction

$$B^{10} + \text{slow neutron} \longrightarrow Li^{7*} + He^{4}$$

which is exoergic to the extent of 2.316 m.e.v.[19]. Here, Li^{7*} denotes Li^{7} left in an excited state to yield ultimately a 0.4-m.e.v. gamma-ray. Such published results have not separated the effects of various types of radiation present in a pile reactor or presented data about the important stress-strain properties of rubber. This paper attempts to fill this gap and to show that by proper choice of isotopic species one may promote vulcanization of rubber in a thermal neutron field to produce a material which is for all intents and purposes free of residual radioactivity.

EXPERIMENTAL

Conventionally mixed compounds containing no chemical curing agents were vulcanized by exposure to thermal neurtons in the T2-H6 position of the thermal column of the Materials Testing Reactor at Idaho Falls, Idaho. Gamma radiation is negligible in this position of the reactor. Any effects can be ascribed entirely to interactions with thermal neutrons. The uncured compounds were pressed into sheets between Holland cloth prior to the dieing out of tensile and swelling specimens. The samples were placed in a graphite sample holder attached to the end of the T2-H6 graphite plug which was modified to permit the flow of helium or air into the sample chamber. The temperature in this region of the reactor is approximately 27° C. Cobalt wires were used as dosimeters, which indicated a thermal (0.025 e.v.) neutron flux of 7.1×10^{9} neutrons/cm^2/sec (nv); the flux was fairly constant from cycle to cycle of reactor operation. Dosages given in nvt units refer to the exposure of rubber compounds to the above flux for a certain period of time in seconds and hence should be considered as "nominal." Rubber compounds containing neutron absorbers, viz., B^{10} and Li^{6}, will, of course, absorb more of the incident radiation.

* Reprinted from *Journal of Polymer Science*, Vol. 43, p. 59 (1960).

The polymer used in this study was a 54 ML-4 butadiene/styrene emulsion copolymer prepared at 5° C in a sulfoxylate recipe and contained 21% bound styrene. The latex was short-stopped with di-*tert*-butyl hydroquinone and stabilized with *N*-phenyl-2-naphthylamine to circumvent residual radioactivity effects upon exposure of the polymer to thermal neutrons.

Boron nitride (obtained from Norton Company, Worcester 6, Mass.), which had been found previously to be a reinforcing agent for rubber[18], was used as source of B^{10}. Boron nitride had a surface area of 10.8 m^2/g.

Lithium methoxide, our source of Li^6, was prepared by dissolving lithium wire in methyl alcohol. The precipitate was decanted and comminuted by ball milling in a *n*-heptane suspension. Finely divided, neutron-absorbing particles are desirable because of the short range of the internally generated ionizing particles and the adverse effect of large particles on the stress-strain properties of rubber.

Physical testing of vulcanizates was carried out by well known procedures. Degrees of net crosslinking were estimated by the equilibrium swelling method in *n*-heptane solution[20].

GENERAL PRINCIPLES

The absorption of neutrons by matter takes place according to the following law:

$$-dI/dx = \sigma n I \tag{1}$$

where I is the intensity of the neutron beam, x the absorber thickness, n the number of nuclei per unit volume in the absorber, and σ is the capture cross section, a constant characteristic of the ability of a nucleus to capture neutrons. Reference to General Electric Chart of Nuclides[32] shows that there is negligible interaction between organic systems because of very small capture cross sections for thermal neutrons. However, the effect obtained in organic systems, e.g., crosslinking, can be noticeably promoted by incorporation of B^{10} or Li^6. Such promotion depends on favorable capture cross sections coupled with the release of energetic, highly ionizing particles according to the following equations:

$$B^{10} + n \longrightarrow Li^{7*} + He^4 \qquad Q = 2.316 \text{ m.e.v.}^{19} \tag{2}$$

$$Li^6 + n \longrightarrow H^3 + He^4 \qquad Q = 4.788 \text{ m.e.v.}^{21} \tag{3}$$

Preliminary tests showed that boron nitride and lithium methoxide were free of induced residual radioactivity after being placed in a thermal neutron field, a requirement for practical application.

The general statistical principles involved in radiation crosslinking have been considered by Charlesby[8,22]. Conditions were examined under which scission of main chain bonds in a long chain polymer, causing a decrease in molecular weight, can yield a crosslinked network. It is generally assumed that ionizing radiation produces crosslinks by removal of hydrogen atoms from neighboring chains, leaving free radical sites which recombine to form tetrafunctional crosslinks. A trifunctional endlink is formed if the polymer radicals resulting from scission can attack neighboring chains and add to them. A gel network will result if both of the radicals resulting from main chain scission are capable of forming endlinks. Chain branching and large increases in weight-average

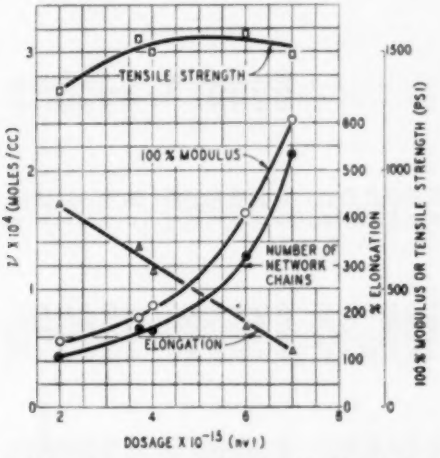

FIG. 1.—Effect of thermal neutron irradiation of a cold rubber tread stock containing boron nitride (0.3 mhr) in a helium atmosphere.

molecular weight can occur if only one of the two radicals arising from each scission is capable of undergoing endlinking, but a gel network will not occur.

Carbon black-filled (Philblack-O), vulcanizates were studied to ascertain the effects of internally generated ionizing particles on technologically important properties of butadiene/styrene rubber. Filler effects can, of course, be expected to complicate the situation.

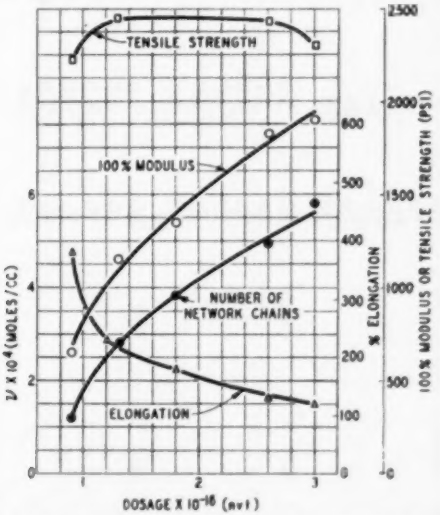

FIG. 2.—Effect of thermal neutron irradiation of a cold rubber tread stock containing lithium methoxide (0.4 mhr) in a helium atmosphere.

TABLE I

PROMOTION OF VULCANIZATION OF COLD RUBBER TREAD STOCK IN A THERMAL NEUTRON FIELD[a]

Promoter	Promoter loading, mhr[b]	Atmosphere	Dosage, mvt $\times 10^{-15}$	100% modulus, psi[c]	Tensile strength, psi[c]	Elongation, %[c]	V_r[d,e]	$\nu \times 10^4$[d] moles/cc	G, crosslinks/ 100 e.v.[e]
None		He	9	*90*	*90*	*380*	0.1374	0.10	—
		He	13	*100*	*100*	*420*	0.1348	0.10	—
		He	18	*90*	*110*	*470*	0.1502	0.12	—
		He	26	*90*	*150*	*560*	0.1610	0.14	—
		He	30	*110*	*160*	*520*	0.1643	0.14	—
		Air	18	*90*	*120*	*550*	0.1463	0.11	—
BN	0.2	He	2.0	180	930	460	0.2535	0.35	0.76
		He	3.7	260	1320	420	0.3047	0.56	0.75
		He	4.0	320	1300	350	0.3125	0.60	0.76
		He	6.0	580	1490	210	0.3785	1.08	0.99
		He	7.0	860	1440	160	0.4348	1.80	1.47
		Air	4.0	410	1500	300	0.3779	1.08	1.48
BN	0.3	He	2.0	280	1340	430	0.2789	0.44	0.69
		He	3.7	380	1560	340	0.3243	0.66	0.61
		He	4.0	430	1500	290	0.3260	0.67	0.58
		He	6.0	820	1580	170	0.3953	1.27	0.79
		He	7.0	1210	1490	120	0.4534	2.15	1.18
		Air	4.0	580	1530	230	0.3934	1.25	1.16
BN	0.4	He	2.0	330	1560	410	0.3145	0.61	0.77
		He	3.7	460	1630	290	0.3540	0.86	0.62
		He	4.0	500	1510	260	0.3563	0.87	0.58
		He	6.0	1040	1620	130	0.4307	1.75	0.83
		He	7.0	—	1470	90	0.4804	2.70	1.12
		Air	4.0	780	1520	190	0.4247	1.68	1.19

TABLE I—(*Continued*)

Promoter	Promoter loading, mhr[b]	Atmosphere	Dosage, nvt $\times 10^{-18}$	100% modulus, psi[c]	Tensile strength, psi[c]	Elongation, %[c]	V_r[d,e]	$\nu \times 10^4$[f] moles/cc	G, crosslinks/ 100 e.v.[g]
$LiOCH_3$	0.2	He	9	330	1720	470	0.3270	0.68	2.0
		He	13	500	2000	380	0.3995	1.33	2.9
		He	18	760	2250	270	0.4531	2.15	3.5
		He	26	890	2290	240	0.4693	2.45	2.8
		He	30	890	2200	230	0.4828	2.75	2.7
		Air	18	650	2380	330	0.4061	1.41	2.3
$LiOCH_3$	0.3	He	9	460	1930	440	0.3706	1.00	2.1
		He	13	790	2350	290	0.4526	2.15	3.3
		He	18	1020	2110	210	0.4684	2.44	2.7
		He	26	1310	2310	180	0.5194	3.80	2.9
		He	30	1360	2320	170	0.5395	4.50	3.0
		Air	18	970	2220	240	0.4515	2.11	2.3
$LiOCH_3$	0.4	He	9	650	2230	380	0.3911	1.21	1.9
		He	13	1150	2450	230	0.4851	2.82	3.3
		He	18	1340	2230	180	0.5221	3.85	3.2
		He	26	1830	2440	130	0.5503	4.90	2.9
		He	30	1890	2300	120	0.5685	5.80	2.9
		Air	18	1240	2350	200	0.4743	2.55	2.1

[a] Butadiene/styrene rubber containing 21% bound styrene, reinforced with 50 phr HAF black (Philblack-O).
[b] Moles/100 g rubber.
[c] Italics denote values obtained from atypical stress-strain curves which are characteristic of uncured materials.
[d] Swelled in *n*-heptane.
[e] V_r = fraction of swollen gel which is rubber.
[f] ν = number of network chains.
[g] Calculated after correction for number of network chains due to bound rubber present in uncured samples.

DISCUSSION OF RESULTS

Arnold, Kraus, and Anderson[17] found that the net degree of cross-linking of butadiene/styrene rubber produced by gamma radiation is approximately proportional to dosage. However, Figures 1 and 2 show that, in the case of vulcanization produced by internally generated particles, the relationship is not linear. Explanation of this behavior is deferred to a later part of this section. Of interest to the radiation chemist are the G values, which in this case are defined as the number of net crosslinks formed per 100 e.v. of energy absorbed. The values shown in Table I and illustrated in part in Figure 3 neglect the contribution of fillers, chain entanglements, and absorption of energy within the fissionable filler particles. Irradiations in a helium atmosphere show that the energy generated within the particles of lithium methoxide is utilized more

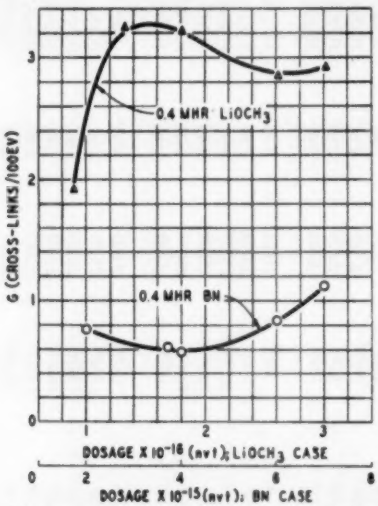

FIG. 3.—Effect of dosage on energy utilized to produce crosslinking in a cold rubber tread stock by thermal neutrons in a helium atmosphere.

efficiently by the rubber matrix than that generated within boron nitride. If it is assumed that the two types of particles are of the same size, the results are consistent with the notion that, because of the potential absorption and degradation of excitation energy by the resonating structure of boron nitride and/or the lower penetrability of the B^{10} reaction products, less energy is available to the rubber *per se* to induce crosslinking. In addition, the resonance structure of boron nitride will tend to lower the ratio of crosslinking to scission by stabilization of free radicals produced by scission. On the other hand, generation of methyl and methoxy fragments from the surface of the lithium methoxide particles may also serve to give *G* values which compare with those obtained in the gamma ray-induced vulcanization of a similar butadiene/styrene rubber[17].

Table I and Figures 1 and 2 summarize the results concerning the response of the butadiene/styrene treadstock to vulcanization by heavy, highly ionizing particles generated internally in a thermal neutron field. The rubber tread stock remained uncured throughout the entire dosage range employed in this study in the absence of B^{10} or Li^6.

The lack of response of the rubber/black masterbatch, as indicated by stress-strain and swelling results, is consistent with negligible interaction of organic systems with thermal neutrons. However, introduction of boron nitride or lithium methoxide into the rubber/black masterbatch produced vulcanization with negligible residual radioactivity as a result of the thermal neutron-induced exoergic reactions described earlier. The difference in nominal dosage requirements with the two promoters reflects the lower capture cross section and isotopic abundance of Li^6 compared to B^{10} when the parent masterbatch contains the same mole percentage of boron nitride and lithium methoxide. The response of the same masterbatch to the different ionizing particles generated in the two neutron absorbers was considerably different. The optimum stress-strain properties of the vulcanizates obtained with Li^6 promotion are comparable with those obtained with gamma rays[17] and considerably superior to those obtained with B^{10} promotion. Promotion by B^{10} is less efficient and the impact of

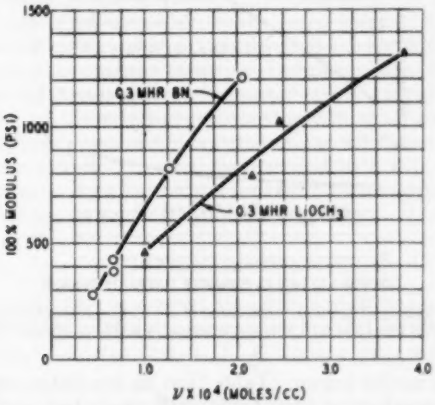

FIG. 4.—Number of network chains vs. 100% modulus in various cold rubber tread stocks.

its energetic particles on the concomitant crosslinking and scission reactions produces a decidedly different vulcanizate. One would anticipate that for the same crosslinking level, as determined by the swelling technique, vulcanizates produced by the two types of promoters should have the same response in 100% modulus. However, Figure 4 shows that this is not the case. It is felt that the difference in response of the two systems indicates a molecular weight difference. The ratio of crosslinking to scission was less with boron nitride promotion than with lithium methoxide. Such a postulate is consistent with the observation that, for the same crosslinking level, the 100% modulus varies inversely with molecular weight[20]. A disparity in moecular weight would also explain the 1000-psi difference in optimum tensile strength of vulcanizates produced by the somewhat analogous promoters.

Figures 1 and 2 show the variations of induced crosslinking with nominal dosage. In the case of lithium methoxide promotion, there is an observable induction period. Such behavior might be evidence for concomitant crosslinking and endlinking. Endlinking predominates in the early stages of irradiation to increase the molecular weight without formulation of a gel network[22]. Crosslinking predominates in the later stages of irradiation. An

infinite network is produced in rubber by the $B^{10}(n, \alpha)Li^{7*}$ reaction with no appreciable induction period, and the introduction of crosslinks increases rapidly in the later stages of irradiation. It is plausible that with boron nitride promotion there is a gradual decrease in the sites available for stabilization of free radicals resulting from main chain fracture on the surface of the particle. As a result, these would be an accelerating influence on the net crosslinking of the rubber.

Figure 5 shows that net crosslinking of rubber approximates a linear relation with loading of the neutron absorbing particles, a result consistent with eq. (1).

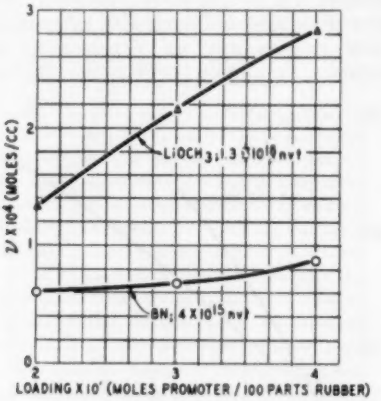

FIG. 5.—Effect of loading of promoter on number of network chains induced in a cold rubber tread stock by thermal neutrons in a helium atmosphere.

Substitution of air for helium (Table I) as an irradiation atmosphere causes a *decrease* in net crosslinking with $Li^6(n, \alpha)H^3$ promotion and an *increase* with $B^{10}(n, \alpha)Li^{7*}$ promotion. The response observed with lithium methoxide is consistent with the findings of others[17,23–29]. Stabilization of polymer radicals by oxygen accentuates scission. The accelerating influence of oxygen observed with boron nitride promotion is similar to the experience of Bach[31] with the x-ray-induced autoxidation of benzene and toluene. A resonance structure tends to absorb and degrade the excitation energy; it also stabilizes free radicals and increases their yield. A mechanism of radical formation at the surface of the boron nitride particles assumes that the chain propagating characteristics of such radicals overwhelm the concomitant stabilization of chain scission in the rubber matrix by direct action with oxygen.

CONCLUSIONS

The nuclear reactions $B^{10}(n, \alpha)Li^{7*}$ and $Li^6(n, \alpha)H^3$ can be used to generate highly ionizing particles in a pure thermal neutron field to vulcanize an otherwise transparent rubber compound. Vulcanizates have satisfactory physical properties comparable with those produced by other means of vulcanization, e.g., gamma rays and peroxides. Such vulcanizates possessed negligible residual radioactivity. The somewhat analogous initiating systems gave vastly different vulcanizates with the same parent rubber compound in a helium at-

mosphere, and a possible explanation is presented. The G values for lithium methoxide promotion (ca. 3) are comparable with those obtained with gamma-ray vulcanizates. Promotion is less efficient with boron nitride, the average values of G being approximately 0.9. The irradiation atmosphere has a pronounced influence on the type of vulcanizate produced and on the energy utilization. Substitution of air for helium as the irradiation atmosphere increases net crosslinking of cold rubber with boron nitride promotion, while it decreases it when lithium methoxide is used as the promoter.

SYNOPSIS

Vulcanization of butadiene/styrene rubber in a thermal neutron field is described. Tread type vulcanization produced from highly ionizing particles resulting from the nuclear reactions $B^{10}(n, \alpha)Li^{7*}$ and $Li^{6}(n, \alpha)H^{3}$ (where Li^{7*} denotes Li^{7} left in excited state to yield ultimately a 0.4 m.e.v. gamma ray) have negligible residual radioactivity and possess physical properties comparable with those produced by other means, e.g., gamma rays and peroxides. Swelling and stress-strain properties indicate that the response of the tread type compound to analogous nuclear reactions have pronounced differences. The vulcanizates also differ markedly. Values of G, the crosslinking efficiency of energy utilization, of the tread-type compound in a helium atmosphere was found to have an average value of 3 for promotion by lithium methoxide and 0.9 in the case of boron nitride. Such values *decrease* 30% with lithium methoxide promotion and *increase* by a factor of 2 for boron nitride promotion when air is substituted for helium as an irradiation atmosphere.

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DIISOCYANATE-LINKED POLYMERS. II. MECHANICAL AND SWELLING PROPERTIES OF SOME POLYURETHANE ELASTOMERS *

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INTRODUCTION

In recent years, as a result of pioneering work in Germany[1] and England[2], diisocyanate-linked polymers have assumed increasing industrial importance. Special interest is being shown in elastomers and foams, although studies of fibers and plastics are continuing. These several classes of diisocyanate-linked polymers, with their markedly different mechanical properties, are possible because substances having two or more groups containing active hydrogen can potentially be linked by diisocyanates to yield a polymer. Since a great number of such substances exist, data which show relationships between polymer structure and mechanical properties have practical importance as well as theoretical interest.

The first paper[3] of this series on diisocyanate-linked polymers discussed the dilute solution properties of linear polymers prepared from toluene-2,4-diisocyanate and polyoxypropylene glycol 2025 (PPG). This paper discusses the properties of one class of diisocyanate-linked elastomers prepared by a one-step cast technique[4], i.e., all reactants are mixed together initially and then allowed to cure. Although these polyurethane elastomers have relatively poor mechanical properties as compared with certain other types of polyurethane elastomers, they are useful in applications where high tensile strength, tear resistance, and ultimate elongation are not required. They also constitute a class of polyurethane polymers convenient for use in studying relationships between chemical structure and mechanical properties.

The elastomers studied were prepared from different ratios of polyoxypropylene glycol 2025 (PPG) and dipropylene glycol (DPG), trimethylol propane (TMP), and either toluene-2,4-diisocyanate (TDI) or hexamethylene-1,6-diisocyanate (HDI). Such elastomers are somewhat different from many others in that the glass transition temperature T_g and the crosslinking density can readily be varied independently. Thus the mechanical properties at any given temperature, being controlled mainly by these two quantities, can be varied markedly by compositional changes.

In the series of elastomers studied, the crosslinking density and T_g were varied independently. Both time-dependent and time-independent (equilibrium) mechanical properties were obtained by measuring tensile stress-strain curves over a wide range of temperatures with an Instron tensile tester. In

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addition, equilibrium swelling ratios in benzene were measured and, simultaneously, rough values for the per cent sol were obtained.

EXPERIMENTAL PROCEDURES

MATERIALS

Polyoxypropylene glycol.—Two different lots of resin-grade (Niax) polyoxypropylene glycol 2025 (PPG), obtained from Union Carbide Chemicals Co., South Charleston, West Virginia, were used. After degassing, the first lot of PPG contained 0.01% or less of water, 1.09×10^{-3} moles of hydroxyl groups/g, 2.7×10^{-5} moles/g of carbon-carbon double bonds, and 1.0×10^{-5} moles/g of carbonyl groups. The hydroxyl content corresponds to an average molecular weight of 1835, assuming all molecules were difunctional. However, the carbon-carbon double bonds appear to replace hydroxyl groups, so that about 5 mole-% of the PPG was monofunctional. If the monofunctional material is considered, the average molecular weight calculated from the amount of hydroxyl was 1790.

The second lot had a molecular weight, calculated from hydroxyl analysis, of 2020. However, enough dipropylene glycol was added to reduce the average molecular weight to the same value as the first lot. The unsaturation was 3.2×10^{-5} moles/g, and the carbonyl was 1.0×10^{-5} moles/g. This second lot was used only in preparing the HDI elastomers in which the crosslinking density was varied.

Dipropylene glycol (DPG).—This material, also obtained from Union Carbide Chemicals Co., was degassed for 2 hr at 80–90° C under 2–3 mm Hg pressure before use.

1,1,1-Trimethylol propane—(TMP).—This material (a product from Matheson, Coleman and Bell, Inc., East Rutherford, New Jersey) was used as received, except that it was ground and then stored in a desiccator over P_2O_5.

Toluene-2,4-diisocyanate (TDI).—Hylene T (E. I. du Pont de Nemours and Co., Inc., Wilmington, Delaware), which is essentially all 2,4 isomer, was distilled and then stored in the absence of moisture until used.

Hexamethylene-1,6-diisocyanate (HDI).—This material, obtained from Mobay Chemical Co., New Martinsville, West Virginia, was distilled and found by isocyanate analysis to be better than 99% pure HDI.

ELASTOMER PREPARATION

The required amounts of PPG, DPG, and TMP were weighed into a round-bottomed flask fitted with a take-off adapter and stopcock, and then heated to 80–90° C under 1–2 mm Hg while being stirred with a magentic stirrer. This procedure gave a final degassing to the materials and also melted and dissolved the TMP, which is a solid below 30° C. Ferric acetylacetonate, a catalyst for urethane formation suggested by Peterson[5], was added to the diisocyanate and the solution then degassed at ambient temperature. This solution was then added to the degassed mixture of other ingredients, care being taken to avoid introducing bubbles. This final mixture was cast into Teflon-coated trays to give sheets about 0.125 inch thick and then cured in a closed laboratory oven at 60° C for 72 hours, the resulting product being a transparent and bubble-free elastomer.

During cure, air and moisture were not excluded, and separate experiments showed that somewhat different properties were obtained by curing under either nitrogen or vacuum. However, in curing the various elastomers, prob-

ably nearly the same amounts of moisture and air were absorbed, so that the different elastomers probably can be compared.

TENSILE TESTING

Tensile stress-strain data were obtained on the elastomers at a series of temperatures by use of an Instron tensile tester equipped with a constant-temperature box which surrounded the crosshead and grips. Dumbbell-shaped tensile specimens were die-cut from the sheets of elastomer and clamped in the Instron by a pair of self-tightening grips. Tensile specimens of two lengths were used: the longer specimen had a 0.50 × 2.25-in gage section, and the shorter specimen had a 0.25 × 1.0 in gage section. However, in calculating elongations from crosshead displacements, effective gage lengths of 3.2 and 1.8 in, respectively, were used. In a separate study made to determine the effective gage length of the longer tensile specimen, it was found that the effective gage length remained constant for elongations up to 150% or more, but that it decreased somewhat as higher elongations were reached. Thus, modulus data calculated from the observed force and crosshead displacement are probably accurate, but elongations at break are undoubetdly somewhat high. The shorter tensile specimen was used only when the elongations were greater than about 500%, and these elongations are probably less reliable than those obtained when the longer specimen was used. The effective gage length of the shorter specimen was determined by comparing Instron data on the same material obtained from both types of tensile specimens.

Tensile measurements were made at crosshead speeds of 10 in/min when the longer tensile specimen was used, and 5.0 in/min when the shorter tensile specimens were used. These speeds gave strain rates of about 3.1 and 2.8 min^{-1}, respectively.

EQUILIBRIUM SWELLING AND SOL FRACTION

The equilibrium swelling in benzene was determined, together with an estimate of the sol fraction. Small pieces of the elastomers were weighed and then immersed in benzene. After four days, the swollen pieces were removed, blotted with filter paper, and reweighed. The benzene was then removed by heating at 55–60° C under vacuum overnight, and the samples were weighed again. The difference between this weight and the initial weight was taken as the weight of sol. It is known that all of the sol was not extracted by this simple technique, especially when the sol fraction was relatively large. However, a useful and semiquantitative measure of the sol fraction was obtained.

The swelling ratio q_m equals V/V_0, where V is the volume of the swollen sample and V_0 the volume of unswollen sample after the sol was removed. This ratio was calculated from the weight of the swollen sample and the weight after the benzene was removed on the basis of the known densities of benzene and resin. The densities of some of the elastomers were measured and found to increase slightly with the concentration of urethane groups. Densities from plots of these data were used.

ANALYSIS OF TENSILE DATA

Various types of information regarding the mechanical properties of elastomers can be obtained from stress-strain curves measured at constant strain rates and at various temperatures. (Actually, measurements are usually made at

a constant crosshead speed which approximates a constant strain rate, especially at elongations less than 100–200%). Such data give the time-dependent, linear viscoelastic properties, as shown previously in studies made with polyisobutylene[6] and SBR rubber[7]. The study of the SBR rubber also showed that the time (strain rate) and temperature dependence of the tensile strength and ultimate elongation can be obtained. Both studies showed that the data obtained at different strain rates and temperatures can be superposed to give composite or master plots reduced to a standard temperature. From such plots, the small deformation behavior can be calculated under a variety of experimental conditions at any temperature above the glass transition temperature T_g[8], and the ultimate properties can be predicted at any strain rate and any temperature above T_g.

The time-temperature reduction scheme is applicable only as long as crystallization does not occur. When crystallization occurs, either before a sample is stretched or during a tensile test, the basic nature of the polymeric network is changed. The size, shape, and number of crystalline areas depend in some complicated manner on the thermal history of the sample and also on the manner in which the sample is tested. Thus, the discussion given here is, in general, applicable only when crystallization does not occur.

Equilibrium values of the modulus and quasi-equilibrium values of the tensile strength and ultimate elongation can also be obtained from stress-strain curves measured at suitable strain rates or temperatures. In obtaining these values, it is necessary to have criteria which show whether given stress-strain data actually represents equilibrium behavior. Since stress-strain curves for elastomers are nonlinear, it is desirable first to linearize them, at least up to moderate elongations, in order to obtain a precise value for the modulus.

The kinetic theory of rubberlike elasticity[9] predicts that the tensile stress-strain curve is given by the equation

$$S = (\nu_e/V)RT(\alpha - 1/\alpha^2) \tag{1}$$

where S is the stress based on the original cross-sectional area of a tensile specimen, ν_e/V is the moles of effective chains per unit volume, R is the gas constant, T is the absolute temperature, and α is the principal extension ratio. (The quantity α is $\gamma + 1$, where γ is the nominal strain and equals $\Delta l/l_0$, Δl being the increase in length and l_0 the initial length.) The kinetic theory also shows that $(\nu_e/V)RT$ equals the shear modulus G. Thus, G equals the slope of a plot of S vs. $\alpha - 1/\alpha^2$; the Young's modulus E, which for elastomers is $3G$, equals the initial slope of a plot of S vs. γ.

Actually, the kinetic theory expression [Equation (1)] usually does not represent quantitatively an experimental stress-strain curve. However, for most elastomers, a plot of αS vs. γ does give a straight line for elongations up to about 100% or even more, and the slope, which can be determined precisely, equals E. The value of E obtained in this manner usually is quite close to $3G$, where G is obtained from the slope of a plot of S vs. $\alpha - 1/\alpha^2$.

The equation $\alpha S = E\gamma$, which can be written in the equivalent form $S = E(1 - 1/\alpha)$, is rather empirical. However, if both sides of Equation (1) are multiplied by α and then $\alpha^2 - 1/\alpha$ is expanded in a power series, the following results:

$$\alpha S = 3G[\gamma + (\gamma^2/3) - (\gamma^4/4) + \cdots] \qquad 0 < \gamma < 1 \tag{2}$$

For values of γ up to 0.5, Equation (2) shows that αS is directly proportional to γ within an error of about 4%. When experimental data are used, plots of αS vs. γ often show even less deviation from linearity, since the kinetic theory equation does not accurately represent the experimental data.

Now that a method has been given for evaluating the modulus E, several methods can be suggested for determining when a modulus is an equilibrium or near-equilibrium value.

First, the strain rate can be varied by factors of 10–1000, and, if the modulus is independent of the strain rate, it appears safe to conclude that a near-equilibrium value has been obtained.

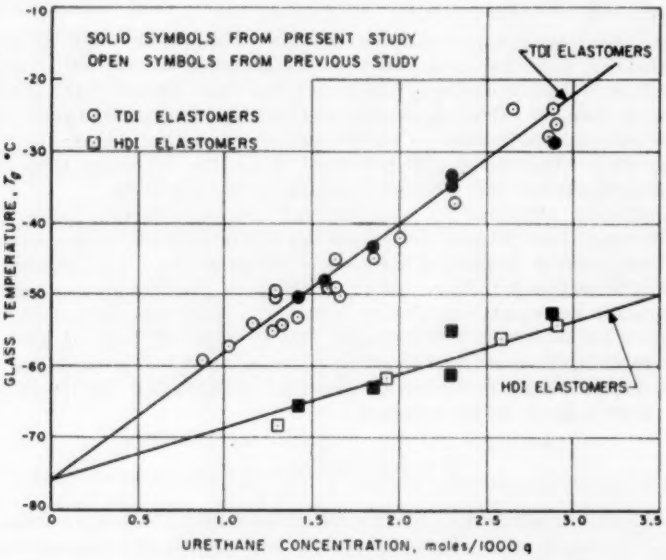

FIG. 1.—Glass temperature T_g of elastomers plotted against the concentration of urethane groups.

Second, the temperature at which the measurement is made can be increased. If the modulus is directly proportional to the absolute temperature, as predicted by the kinetic theory, it is an equilibrium value. Actually, if the modulus remains constant or increases only slightly with temperature, it is probably close to its equilibrium value.

Third, the stress-strain data can be plotted as log αS vs. log γ. If the slope of this plot is unity, the data probably closely represent equilibrium conditions. This statement is based on the fact that for elastic response the exponent n in the equation

$$\alpha S = E\gamma^n \tag{3}$$

is unity, and for viscous response the exponent n is zero; i.e., for a Newtonian fluid the stress is independent of the deformation and depends only on the strain rate or velocity gradient. In the studies made with polyisobutylene[6] and an SBR rubber[7], the exponent n decreased from 1.0 to 0.6–0.5 as the temperature

was decreased or as the strain rate was increased. As the temperature was decreased further, the exponent increased; it should approach a value near unity when the behavior of the material approaches that typical of glassy material.

Although the modulus of a crosslinked elastomer reaches an equilibrium value at sufficiently high temperatures or sufficiently low strain rates, the tensile strength and ultimate elongations apparently do not decrease to definite equilibrium values[7]. However, the strain-rate dependence of these ultimate properties becomes quite small at elevated temperatures. Thus, it seems convenient to speak of quasi-equilibrium values for the tensile strength and ultimate elongation.

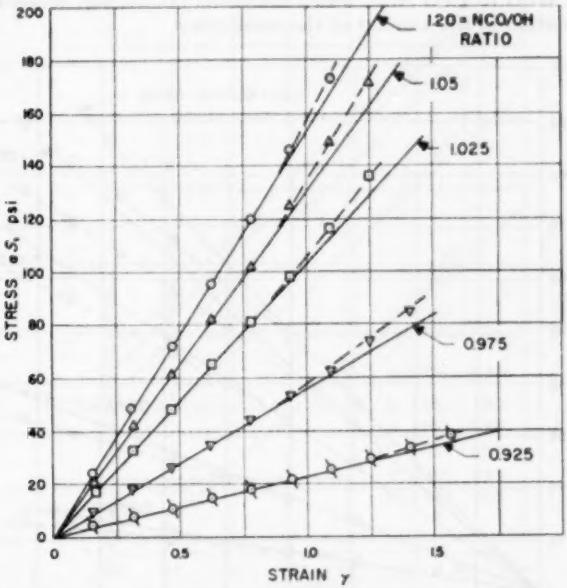

FIG. 2.—The stress αS plotted against strain for a series of TDI elastomers having different NCO/OH ratios.

The tensile strength always increases when the strain rate is increased or the temperature is decreased. On the other hand, the ultimate elongation passes through a maximum with decreasing temperature or, equivalently, increasing strain rate. At low temperatures (temperatures in the vicinity of T_g), cold-drawing or necking of a tensile specimen often occurs, making the tensile strength and ultimate elongation data difficult to interpret. Since cold-drawing is associated with a temperature gradient at the neck, the stress-strain data do not show isothermal properties.

EXPERIMENTAL RESULTS AND DISCUSSION

GLASS TRANSITION TEMPERATURE

The glass transition temperature T_g of elastomers prepared with either TDI or HDI increases linearly with the concentration of urethane groups [U],

expressed here as moles per kilogram. Figure 1 shows data obtained on a large number of elastomers, including some of the elastomers described in this paper, and also other elastomers prepared in earlier studies (unpublished). The measurements were carried out in a glass dilatometer containing Dow-Corning 200 silicone fluid as the confining liquid. No effort was made to obtain highly precise data, and some of the individual values may be in error by a few degrees. However, the large number of points quite accurately fit the straight lines drawn. Both lines extrapolate to $-76°$ C at [U] = 0. This value should represent T_g for a high molecular weight polyoxypropylene glycol. The wide range of [U] was obtained by use of PPG of different molecular weights, by addition of DPG to PPG 2025, which decreased the average molecular weight, and by variation in the amount of the crosslinker.

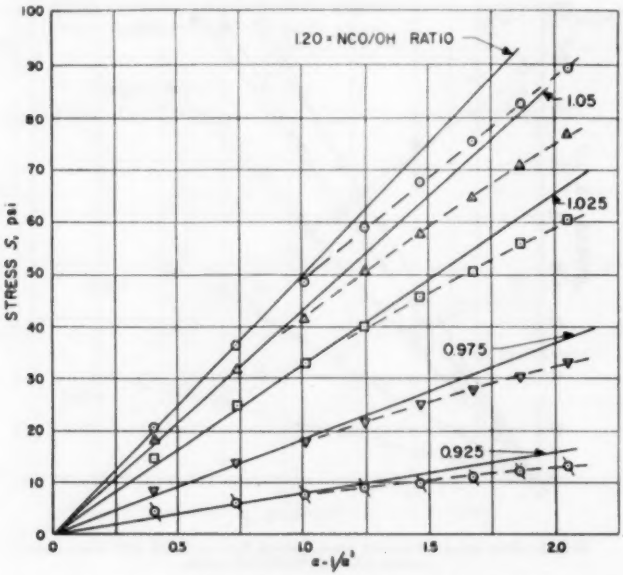

FIG. 3.—The data shown in Figure 2 plotted as S vs. $\alpha - 1/\alpha^2$.

Although T_g for both types of elastomers increases linearly with [U], the rate of increase is considerably greater for those prepared with TDI than for those prepared with HDI. For the TDI-containing elastomers, the increase of T_g with [U] is no doublt largely due to the increase in chain stiffness produced by the increase in concentration of phenylene groups. Such an effect has been clearly shown by Edgar[10] who studied a series of mixed polyesters of polyethylene terephthalate. He showed that T_g increases linearly with the number of *p*-phenylene groups per 100 aliphatic chain atoms and that this relationship holds over a range of 160°. This variation of T_g was attributed primarily to increasing chain stiffness, although it is generally recognized that interchain forces also influence T_g.

Some of the increase in T_g with [U] for the polyurethane elastomers is probably due to increase in interchain forces; as will be seen subsequently, the

cohesive energy density of the elastomers increases with [U]. The increase in T_g for the HDI-containing elastomers is probably largely due to the increase in their cohesive energy density, which is caused by introduction of urethane groups. Thus, several factors may account for the reduction in T_g observed when HDI is substituted for TDI. These are (1) that the aromatic ring in TDI is rigid compared with the hydrocarbon chain in HDI, and (2) that the aromatic ring has a higher cohesive energy density than the hydrocarbon chain in HDI.

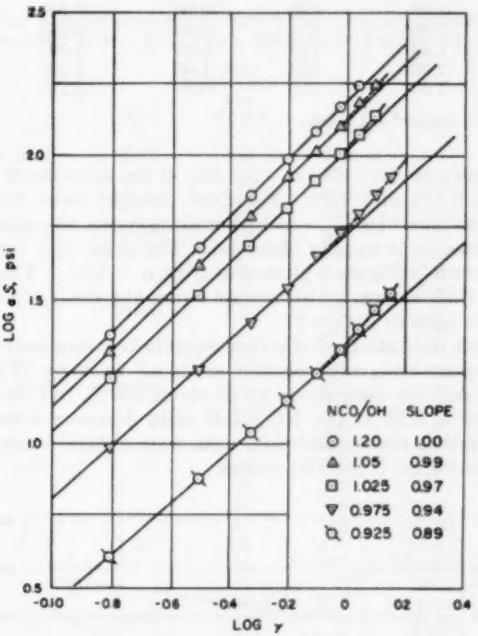

FIG. 4.—The data shown in Figure 2 plotted as log αS vs. log γ.

EFFECT OF NCO/OH RATIO ON ELASTOMER PROPERTIES

The effect of stoichiometry on the properties of elastomers was studied for two reasons: (*1*) the hydroxyl analysis of PPG is accurate to only a few per cent, and in preparing crosslinked polymers it is desirable that exactly equivalent amounts of reacting materials be used; and (*2*) side reactions, including those due to traces of moisture, may occur when polyurethane elastomers are prepared, and such reactions modify the theoretical amounts of materials needed for stoichiometry.

Nine elastomers were prepared, the amount of TDI used being that required to vary the ratio of isocyanate to hydroxyl groups (NCO/OH ratio) from 0.925 to 1.30. In addition to TDI, the elastomers contained PPG and TMP in the molar ratio of 1.0 to 0.25. Tensile stress-strain data were measured at a strain rate of 3.1 min^{-1} at 25° C. Also, equilibrium swelling was measured in benzene together with the per cent sol.

TABLE I

MECHANICAL AND SWELLING PROPERTIES OF TDI ELASTOMERS HAVING DIFFERENT NCO/OH RATIOS

Sample	NCO/OH	E, psi	n	Sol, %	Q_m
1	0.925	23	0.89	29.0	16.9
2	0.950	37	0.95	26.8	14.5
3	0.975	56	0.94	19.7	11.9
4	1.00	80	0.97	13.8	8.97
5	1.025	103	0.97	12.1	8.15
6	1.05	133	0.99	9.24	7.25
7	1.05[a]	131	0.99	7.25	6.83
8	1.10	140	0.99	5.50	6.45
9	1.20	152	1.00	3.52	5.91
10	1.30	151	0.97	3.28	5.82

[a] Duplicate sample prepared and tested.

Figure 2 shows plots of αS vs. γ for five of the elastomers with NCO/OH ratios between 0.925 and 1.20. Excellent straight lines were obtained for elongations up to about 100%. At higher elongations, the experimental points lie above the lines, as is uaually observed. The same data for elongations up to 125% are shown in Figure 3 plotted as S vs. $\alpha - 1/\alpha^2$. The lines have been drawn so that their slopes, which should equal the shear modulus G, equal $\frac{1}{3}$ the slopes of the lines in Figure 2.

To obtain an indication of whether equilibrium stress-strain curves were measured, the same data were plotted as $\log \alpha S$ vs. $\log \gamma$ (Figure 4). Here, straight lines result for elongations up to about 100%, but the slopes decrease from about 1.00 to 0.89 as the NCO/OH ratio decreases from 1.20 to 0.925. Thus it appears that near-equilibrium data were obtained only for the elastomers having the higher NCO/OH values.

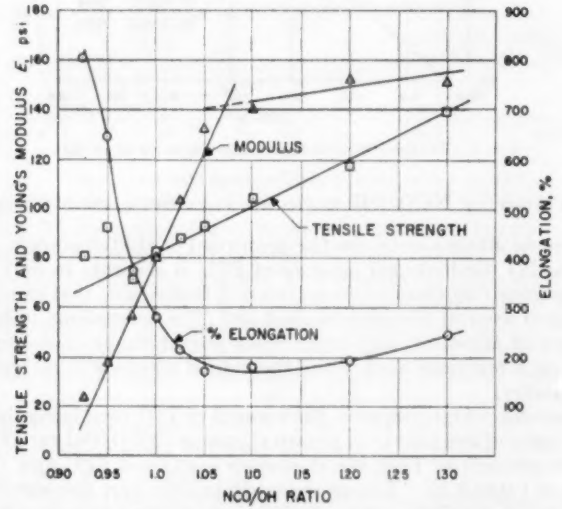

FIG. 5.—The variation of the tensile strength, Young's modulus, and ultimate elongation with the NCO/OH ratio.

Curves similar to those shown in Figures 2, 3, and 4 were obtained for the elastomers having the four other NCO/OH ratios, and the results are given in Table I. The ultimate properties and the modulus E are plotted against the NCO/OH ratio in Figure 5, which shows that these properties vary markedly. However, the modulus and ultimate elongation vary only slightly for NCO/OH ratios greater than 1.05. Thus, all other elastomers to be discussed were prepared at an NCO/OH ratio of 1.10.

TABLE II

MECHANICAL AND SWELLING PROPERTIES OF TDI ELASTOMERS WITH [U] = 2.30, $T_g = -34°$ C AND DIFFERENT VALUES OF ν/V

$\nu/V \times 10^4$	Q_m	Sol, %	Test temperature $(T-T_g)$, °C	E, psi	n	$(298/T)E$
6.35	3.16	0.66	105	440	1.0	381
			83	482	1.0	446
			61	502	1.0	499
			33	708	0.94	776
3.53	3.75	0.50	105	310	1.0	268
			83	312	1.0	289
			61	319	1.0	317
			33	415	0.89	455
2.44	4.22	0.85	105	252	1.0	218
			83	246	1.0	228
			61	250	1.0	248
			33	302	0.87	331
1.87	4.68	1.14	105	200	1.0	185
			83	200	1.0	185
			61	208	1.0	207
			33	305	0.91	334
1.51	5.21	1.28	105	146	1.0	126
			83	160	1.0	148
			61	176	0.96	175
			33	358	0.89	392
1.27[a]	5.19	1.57	105	173	1.0	150
			83	170	1.0	157
			61	170	1.0	169
			33	278	0.85	304
0.79[a]	7.29	3.75	105	92	0.86	80
			83	107	0.88	99
			61	152	0.86	152

[a] Elastomers prepared at a different time.

An indication of why equilibrium modulus values were obtained only for the elastomers prepared at the higher NCO/OH ratios is given in Table I, which shows that the exponent n decreases as the per cent sol increases. To understand the qualitative correlation between n and the per cent sol, we first consider an elastomer containing no sol tested at the strain rate and temperature needed to give an n of almost unity. During the test, the stress operates against both elastic and viscous resistance, although only a negligible proportion of the stress operates against the vicsous resistance, and the overall stress-strain curve is quite similar to one for an ideal elastic material. Now, imagine that a number of valence bonds are broken at random in the sample to yield a certain amount of high molecular weight sol. This structural change reduces the equilibrium modulus of the material but should not change the internal viscosity significantly. When this sample is tested, the stress required to over-

TABLE III

MECHANICAL AND SWELLING PROPERTIES OF HDI ELASTOMERS WITH [U] = 2.30, $T_g = -59°$ C, AND DIFFERENT VALUES OF ν/V

$\nu/V \times 10^4$	Q_m	Sol, %	χ_1	Test temperature $(T-T_g)$, °C	E, psi	n	$(298/T)E$
6.35	3.94	1.95	0.20	130	363	1.0	314
				108	351	1.0	325
				84	326	1.0	326
				63	343	—	369
3.53	4.42	1.89	0.31	130	287	1.0	249
				108	280	1.0	259
				84	266	1.0	266
				63	263	1.0	283
1.87	4.84	2.43	0.41	130	216	1.0	187
				108	208	1.0	192
				84	200	1.0	200
				63	200	1.0	215
1.27	5.67	3.33	0.41	130	165	1.0	143
				108	162	1.0	150
				84	157	1.0	157
				63	167	0.93	180

come the viscous resistance may be rather similar to that required during the first test, but now the stress required to overcome the elastic forces is markedly lower. The net result is that the sample containing sol exhibits a larger viscous response than did the original sample, and the exponent n is reduced. The exponent n thus may show two things: (*1*) whether a stress-strain curve represents essentially equilibrium response, and (*2*) which of two similar samples contains the largest sol fraction.

ELASTOMERS PREPARED FOR STUDY

When the crosslinking density of elastomers prepared from PPG 2025 and a diisocyanate is increased by adding more triol, both the number of chains per unit volume (ν/V) and the glass temperature T_g are changed. (When no

TABLE IV

MECHANICAL AND SWELLING PROPERTIES OF TDI ELASTOMERS HAVING $\nu/V = 1.87 \times 10^{-4}$ AND DIFFERENT CONCENTRATIONS OF URETHANE GROUPS

[U], moles/kg	T_g, °C	Q_m	Sol, %	χ_1	Test temperature $(T-T_g)$, °C	E, psi	n	$(298/T)E$
1.42	−51	6.24	4.28	0.366	100	150	1.0	139
					78	154	1.0	153
1.57	−48	5.92	3.32	0.369	97	165	1.0	153
					75	160	1.0	159
1.85	−43	5.50	2.99	0.392	92	174	1.0	161
					70	166	1.0	165
2.30	−34	4.68	1.14	0.443	105	200	1.0	173
					83	200	1.0	185
					61	208	1.0	207
2.89	−24	4.00	1.10	0.482	95	228	0.97	198
					73	240	0.97	222
					51	286	0.91	284

plasticizer, sol fraction, or dangling chains are present in a crosslinked polymer, $\nu/V = \rho/M_c$ where ρ is the polymer density and M_c is the average molecular weight between crosslinking sites.) The glass temperature increases since the concentration of urethane groups, [U], is increased (see Figure 1). Hence, in an attempt to study the effects of changing T_g and ν/V independently, two series of elastomers were prepared with TDI, and two similar series were prepared with HDI. In one series, ν/V was held constant at 1.87×10^{-4} while [U] was varied from 1.42 to 2.89 moles/1000 g; in another series, [U] was held constant at 2.30 while ν/V was varied. Such compositional changes were made by use of different ratios of PPG to DPG (which varied the average molecular weight of the diol) and the appropriate amount of the triol TMP. Sufficient TDI or HDI was used to give an apparent NCO/OH ratio of 1.10. Tables II–V give some of the properties of these four series of elastomers.

TABLE V

MECHANICAL AND SWELLING PROPERTIES OF HDI ELASTOMERS HAVING $\nu/V = 1.87 \times 10^{-4}$ AND DIFFERENT CONCENTRATIONS OF URETHANE GROUPS

[U], moles/kg	T_g, °C	Q_m	Sol, %	χ_1	Test temperature $(T-T_g)$, °C	E, psi	n	$(298/T)E$
1.42	−65	7.19	4.63	0.327	136	143	1.0	124
					114	138	1.0	128
					90	125	1.0	125
					69	124	0.94	133
1.85	−62	5.52	2.39	0.388	133	191	1.0	165
					111	189	1.0	175
					87	178	1.0	178
					66	173	1.0	186
2.30	−59	4.84	2.43	0.417	130	216	1.0	187
					108	208	1.0	192
					84	200	1.0	200
					63	200	1.0	215
2.89	−55	4.15	2.60	0.452	126	260	1.0	225
					104	242	1.0	224
					80	232	1.0	232
					59	242	0.98	260

When a triol is used as the crosslinking agent, the theoretical value of ν/V, expressed as moles per milliliter, is given by the expression

$$\nu/V = 3 \text{ moles of triol}/2 \text{ ml of elastomer} \tag{4}$$

since each mole of triol contributes 1.5 chains. In this paper, the symbol ν/V will refer to the number of chains per unit volume calculated by use of Equation (4), and ν_e/V will refer to the number of effective chains per unit volume; this latter quantity can be calculated from a measured equilibrium modulus E in the equation

$$E = 3(\nu_e/V)RT \tag{5}$$

where E is the initial slope of the stress-strain curve given by Equation (1). Ordinarily, it is expected (1) that ν/V will equal ν_e/V only if exactly stoichiometric quantities of isocyanate and hydroxyl groups are used, and (2) that no side reactions occur. Both assumptions are not completely true here, since

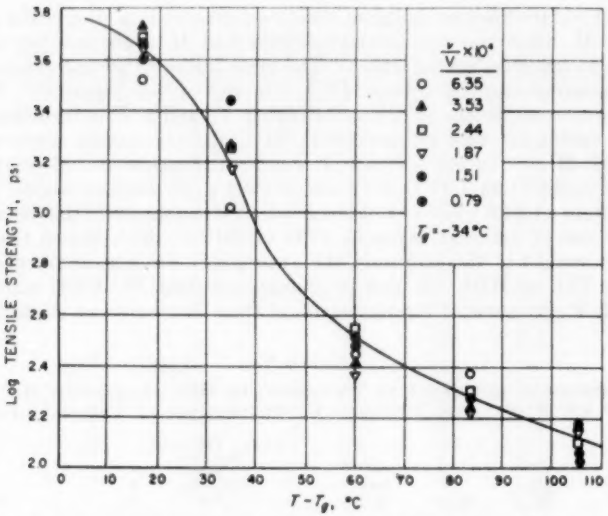

FIG. 6.—The temperature dependence of the tensile strength of a series of TDI elastomers with a urethane group concentration of 2.30 and different values of ν/V.

some excess of isocyanate was used, and side reactions definitely occur, either with atmospheric moisture during cure or with groups other than hydroxyl in the elastomer. Further, the PPG 2025 contains about 5 mole-% monofunctional molecules, which leads to a three-dimensional network containing dang-

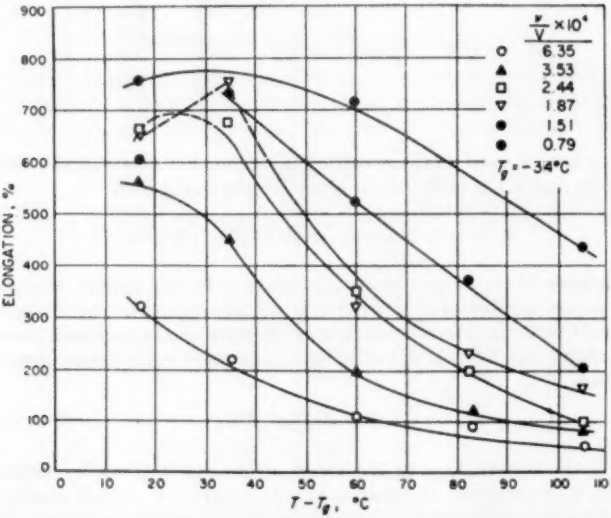

FIG. 7.—The temperature dependence of the ultimate elongation of a series of TDI elastomers with a urethane group concentration of 2.30 and different values of ν/V.

ling chains and some sol fraction. Also, since the ratio of PPG 2025 to DPG was varied in each series of elastomers, the amount of monofunctional material varied within each series. Thus, in general, ν_e/V is less than that calculated from the amount of triol used.

TEMPERATURE-DEPENDENT ULTIMATE MECHANICAL PROPERTIES

The tensile strengths and ultimate elongations of the four series of elastomers are shown in Figures 6–9 and 11–14 plotted against $T - T_g$. Over the

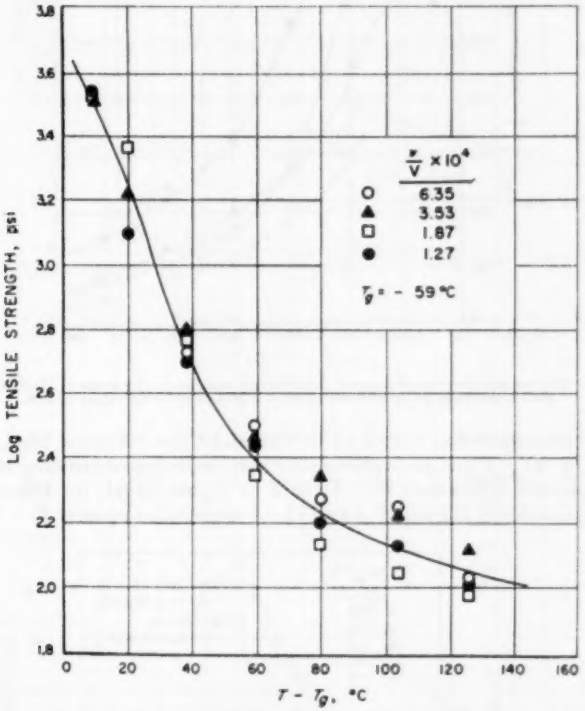

FIG. 8.—The temperature dependence of the tensile strength of a series of HDI elastomers with a urethane group concentration of 2.30 and different values of ν/V.

temperature range covered, both the tensile strengths and ultimate elongations show pronounced changes. Since it has been found that a decrease in temperature is equivalent to an increase in strain rate at a fixed temperature[7], the ultimate properties also depend on strain rate over the temperature ranges shown. Quantitatively, a strain rate R_T at temperature T gives the same effect as a strain rate R_s at a standard temperature T_s when $R_s = a_T R_T$, where a_T is given by the equation of Williams, Landel, and Ferry[11]:

$$\log a_T = - C_1(T - T_s)/(C_2 + T - T_s) \qquad (6)$$

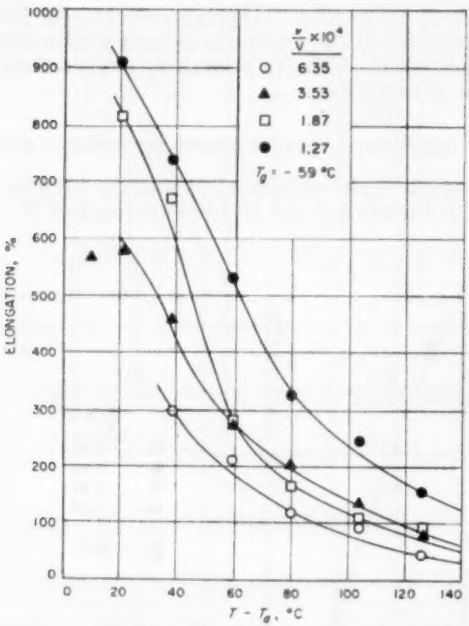

FIG. 9.—The temperature dependence of the ultimate elongation of a series of HDI elastomers with a urethane group concentration of 2.30 and different values of ν/V.

When the near-universal values $C_1 = 8.86$ and $C_2 = 100.6$ are used, T_s closely equals $T_g + 50$. Thus, amorphous polymers are in corresponding states when the temperature differences $T - T_s$ or $T - T_g$ are equal; for this reason, the various quantities in Figures 6–9 and 11–14 are plotted against $T - T_g$ instead

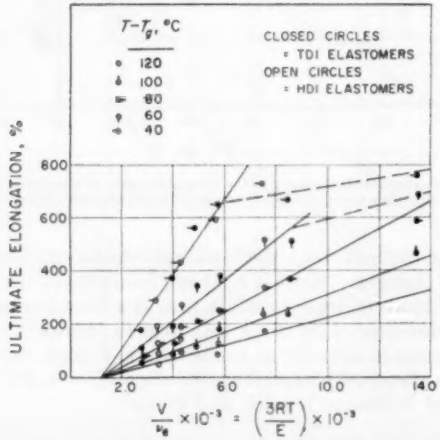

FIG. 10.—Ultimate elongation plotted against V/ν_e for TDI and HDI elastomers having [U] = 2.30 moles/1000 g. (○), HDI elastomers; (●), TDI elastomers.

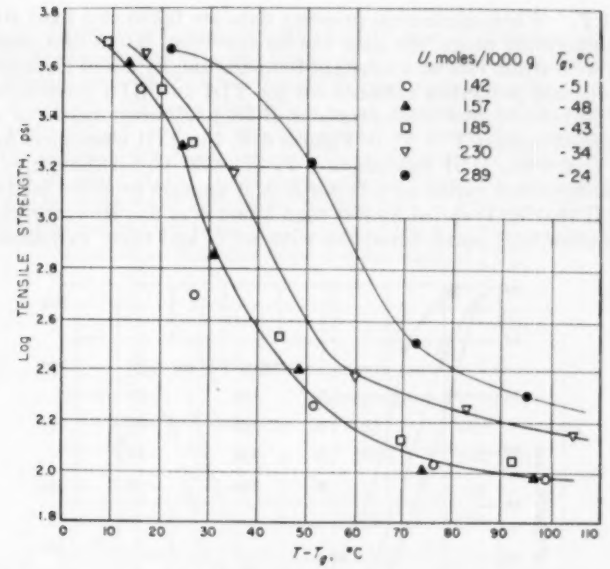

FIG. 11.—The temperature dependence of the tensile strength of a series of TDI elastomers having $\nu/V = 1.87 \times 10^{-4}$ and different concentrations of urethane groups.

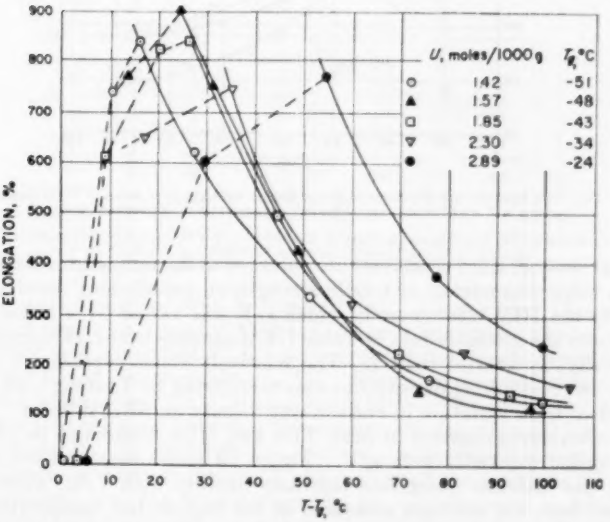

FIG. 12.—The temperature dependence of the ultimate elongation for a series of TDI elastomers having $\nu/V = 1.87 \times 10^{-4}$ and different concentrations of urethane groups.

of against T. When mechanical property data are taken at a fixed strain rate over a temperature range, the data can be converted into a plot showing the variation with strain rate at a constant temperature, by use of Equation (6).

The ultimate properties obtained for the TDI and HDI elastomers having [U] = 2.30 but different concentrations of triol (different values of ν/V) are shown plotted against $T - T_g$ in Figures 6–9; the TDI elastomers have a T_g of −34° C and the HDI elastomers a T_g of −59° C. Although ν/V in the TDI elastomers was varied by a factor of 8, it appears from the modulus data in Table II that ν_e/V varied by less than a factor of 5. However, the tensile strengths show only small variations with ν_e/V, and these variations appear

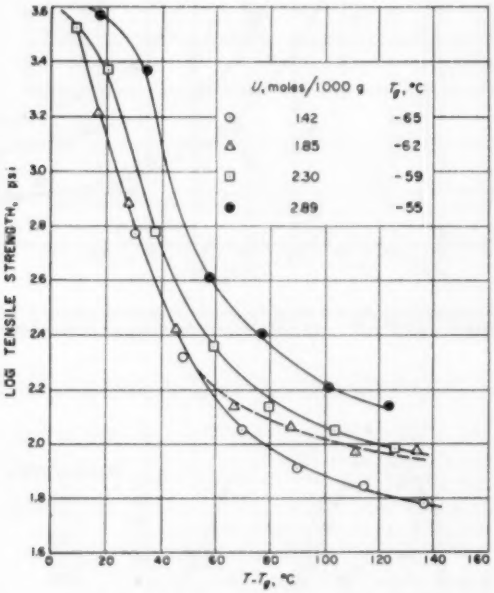

FIG. 13.—The temperature dependence of the tensile strength of a series of HDI elastomers having $\nu/V = 1.87 \times 10^{-4}$ and different concentrations of urethane groups.

somewhat random since crossovers are observed as the temperature is decreased. Also, no large dependence of tensile strength on crosslinking density was observed for the HDI elastomers in which ν/V was varied by a factor of 5, although from the modulus data in Table III, it appears that ν_e/V varied only by a factor slightly greater than 2. The relatively small dependence of tensile strength on crosslinking density has also been found by Epstein[12], who studied the effect of wide variation in crosslinking density on SBR rubbers.

The ultimate elongation of both TDI and HDI elastomers in which [U] = 2.30 varied markedly with ν/V. Figure 10 shows that at fixed values of $T - T_g$, the ultimate elongation increases linearly with V/ν_e, where V/ν_e is calculated from the modulus measured at the highest test temperature. The lines in the figure do not pass through the origin, but intersect the abscissa at a common point. This behavior suggests some systematic error in V/ν_e.

However, the figure does show that both the TDI and HDI elastomers have the same ultimate elongations at equal values of $T - T_g$, and that the rate of increase of elongation with V/ν_e is strongly temperature-dependent. The slope of a line equals the ultimate elongation of an elastomer in the hypothetical standard state of $\nu_e/V = 1$. Thus, the slopes can be plotted against $T - T_g$ to show the temperature dependence of the elongation for elastomers in this hypothetical standard state. In this way, the temperature-dependent elongations for a large number of elastomers having [U] = 2.30 but different cross-linking densities can be summarized. However, the data for elastomers having different [U]-values show that the slope is a function of [U].

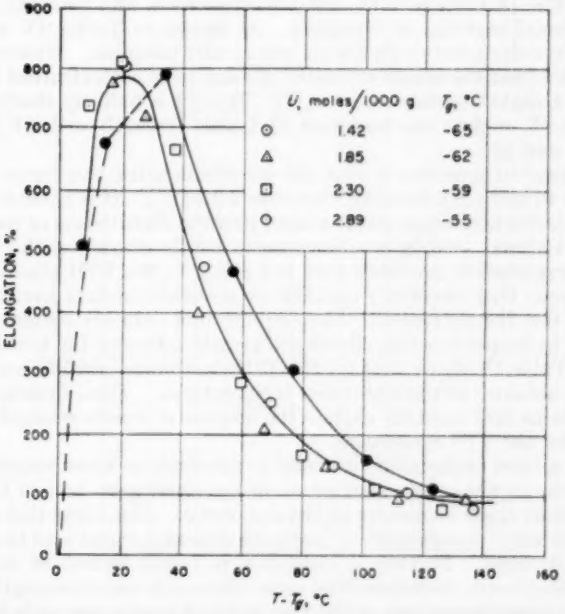

FIG. 14.—The temperature dependence of the ultimate elongation of a series of HDI elastomers having $\nu/V = 1.87 \times 10^{-4}$ and different concentrations of urethane groups.

If the concentration of triol is constant but [U] is varied in a series of elastomers, it might be expected that the ultimate properties plotted against $T - T_g$ would be independent of [U], provided that the specific forces between chains do not depend appreciably on [U]. Figure 11 shows that this is true for the tensile strengths of the TDI elastomers having [U]-values of 1.42, 1.57, and 1.85, but that the tensile strength is markedly greater when [U] is 2.30 and 2.89. Qualitatively, the same effect is observed for the tensile strengths of the HDI elastomers, as shown in Figure 13, although an elastomer with [U] = 1.57 was not prepared, and the tensile strengths for the elastomer in which [U] = 1.85 diverge from the lowest curve at the three highest temperatures. Also, the tensile strengths of the elastomers in which [U] = 2.30 and 2.89 are definitely greater than for the other two elastomers.

It is difficult to explain why tensile strength increases with [U], although several possible explanations can be considered. First, the number of effective chains per unit volume increases with [U], even though all elastomers had the same triol concentration. This increase can be seen from Tables IV and V, which show that the equilibrium modulus, reduced to 298° K, increases from 139 to 198 psi for the TDI elastomers and increases from 124 to 225 psi for the HDI elastomers. (For the TDI elastomers with [U] = 2.89, the temperature dependence of the modulus and the exponent n indicate that a near-equilibrium modulus was not measured. However, the values for the other elastomers, and especially those for the HDI elastomers, appear to be close to equilibrium.) The increase in modulus with [U] is probably due to the fact that to increase [U], the ratio of PPG to DPG must be decreased, and thus the amount of monofunctional material is decreased. As shown in Tables IV and V, this decrease gives elastomers with less sol and greater modulus. However, Figures 6 and 8 show that the tensile strengths of elastomers with identical [U]-values show only a slight dependence on ν_e/V. Thus, it is unlikely that minor variations in ν_e/V explain the variation of tensile strength with [U] shown in Figures 11 and 13.

The second explanation is that the interchain attractive forces—probably due largely to hydrogen bonding—increase with [U]. It is possible that these secondary forces help bring about a more uniform distribution of forces among the network chains, leading to an increase in tensile strength with [U]. However, this explanation probably does not apply to the HDI elastomers, since Table V shows that essentially equilibrium stress-strain data were obtained at the higher test temperatures. When equilibrium data are obtained, it is unlikely that hydrogen-bonding effects will greatly influence the tensile strength. However, Table IV shows that for the TDI elastomers, equilibrium data were not always obtained at the higher test temperatures. Thus, hydrogen bonding between chains may partially explain the increase of tensile strength with [U], especially for the TDI elastomers.

To test a third explanation, it would be necessary to know something about the regularity of the network structure in the elastomers, and to know which bonds are most easily broken by mechanical stress. It is likely that an increase in the uniformity (or regularity) of network structure would lead to an increase in tensile strength. Further, a reduction in concentration of mechanically weak chemical bonds would also lead to an increase in tensile strength.

The ultimate elongations of the two series of elastomers each having constant triol concentration depend primarily on $T - T_g$, as shown in Figures 12 and 14. However, the curve for the elastomers with [U] = 2.89 lies appreciably above the other curve. This dependence of the ultimate elongation on [U] is undoubtedly due to some of the same factors which influence the dependence of the tensile strength on [U]. However, an increase in ν_e/V would be expected to decrease the ultimate elongation, as illustrated in Figures 7 and 9. Since the elongations shown in Figures 12 and 14 increase with [U], this increase seems most likely due to specific attractive forces or to the factors discussed in the previous paragraph.

As the temperature is decreased, the ultimate elongations for all elastomers increase markedly, i.e., from about 100% to 800–900%, and then drop rapidly to a few per cent. Few points on the low-temperature side of the maximum are shown, since cold-drawing often occurred, leading to somewhat meaningless values. However, in the vicinity of T_g, the ultimate elongations were generally very low.

EQUILIBRIUM MODULUS AND SWELLING DATA

Values for Young's modulus E were obtained from the slopes of plots of αS vs. γ and are given in Tables II–V at several test temperatures, expressed as $T - T_g$, ° C. Values of the exponent n in Equation (3), obtained from the linear portion of plots of log αS vs. log γ, are also given. From the tables, it is seen that when $n = 1$ at some temperature, little or no decrease of E occurs when the temperature is increased; but when n is less than unity, the modulus always decreases with an increase in temperature. A modulus value which increases only slightly with a decrease in temperature is considered to be a near equilibrium value. However, an increase in E with increasing temperature is considered to be the best indication that equilibrium values have been obtained.

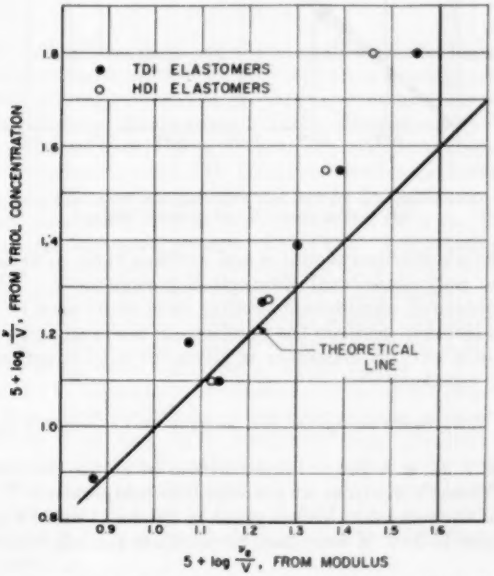

FIG. 15.—Comparison of ν/V calculated from triol concentration with ν'/V calculated from modulus.

The best illustration of such behavior is given in Tables III and V where it is observed that E, for the HDI elastomers, increases with temperature. However, when these E-values are reduced to 298° K by multiplying by the factor $298/T$, the reduced values at the highest test temperatures are roughly constant or show only a slight decrease with an increase in temperature.

For the elastomers having [U] = 2.30, values of ν_e/V were calculated from the modulus values at the highest test temperatures by use of Equation (5). These values of ν_e/V are compared in Figure 15 with values of ν/V calculated from the triol concentration [Equation (4)]. It is seen that ν_e/V obtained from the modulus data is in good agreement with values calculated from the triol concentration, except for elastomers having high triol concentration. However, some data on other polyurethane elastomers suggest that the good agreement observed here may be fortuitous.

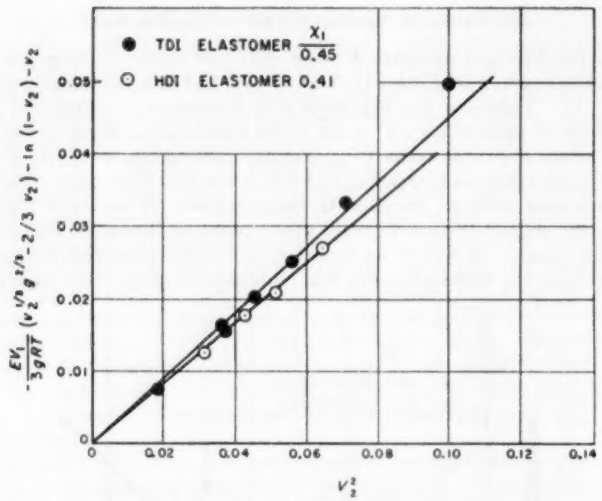

FIG. 16.—Evaluation of χ_1 for TDI and HCI elastomers from equilibrium modulus and swelling data; [U] = 2.30 moles/1000 g.

Values of the equilibrium modulus and swelling ratio in benzene were used to evaluate the polymer-solvent interaction parameter χ_1. Once a reliable value for χ_1 is obtained, equilibrium swelling data alone need be used to obtain ν_e/V. The relationship between the equilibrium modulus and volume fraction of polymer v_2 in a swollen elastomer is given for a tri-functional crosslinked material by the equation[13,14]

$$(-EV_1/3gRT)(v_2^{\frac{1}{3}}g^{\frac{1}{3}} - \tfrac{2}{3}v_2) - v_2 - \ln(1 - v_2) = \chi_1 v_2^2 \qquad (7)$$

where v_2 equals $1/q_m$, g is the volume fraction of gel in the elastomer before swelling, E is Young's modulus at the absolute temperature T and V_1 is the molar volume of the solvent. Values given in Tables II and IV for q_m, per cent sol, and E reduced to 298° K were used to calculate the left-hand side of Equa-

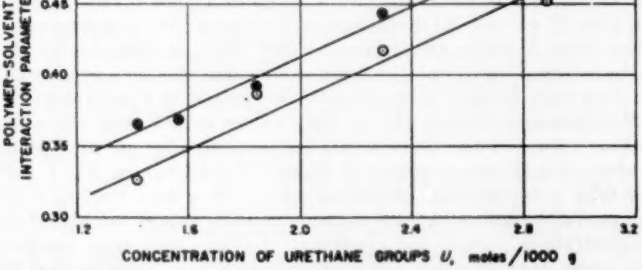

FIG. 17.—The variation of the polymer-solvent interaction parameter χ_1 with the concentration of urethane groups in both TDI and HCI elastomers.

tion (7), which is plotted against v_2^2 in Figure 16. The linear dependence shows that the modulus can be related quantitatively to the swelling data by use of a constant value of χ_1. For the TDI elastomers with [U] = 2.30, χ_1 is 0.45, and for the comparable HDI elastomers, it is 0.41. This decrease in χ_1 is qualitatively predictable, because the cohesive energy density of the hydrocarbon chain in the HDI is lower than that of the aromatic ring in TDI.

Values of χ_1 for elastomers with different [U]-values were calculated by use of Equation (7). The values, given in Tables IV and V, are shown in Figure 17 to vary linearly with [U], within experimental error. Here the lines have been drawn through $\chi_1 = 0.44$ for the TDI elastomer with [U] = 2.30 (a χ-value of about 0.45 was obtained from Figure 16) and through $\chi = 0.41$ for the HDI elastomer having the same value of [U].

SYNOPSIS

A study was made of the mechanical and equilibrium swelling properties of five series of polyurethane elastomers prepared from polyoxypropylene glycol 2025, dipropylene glycol, trimethylol propane, and either toluene diisocyanate (TDI) or hexamethylene diisocyanate (HDI). The study included the dependence of the properties on the ratio of isocyanate to hydroxyl groups, the concentration of urethane groups, [U], and the triol concentration; the triol concentration and [U] were varied independently in four series of elastomers. It was found that the glass transition temperature for both the TDI elastomers and HDI elastomers increased linearly with [U]. For elastomers having a constant [U], the quasi-equilibrium elongation at a given value of $T - T_g$ increased linearly with the reciprocal of the number of effective chains per unit volume, but the tensile strength depended only slightly on this quantity. For elastomers having the same triol concentration, the ultimate properties over a wide temperature range were compared at equal values of $T - T_g$ and were found to depend on [U], especially for elastomers having the largest [U]-values. Several factors that might contribute to this behavior are considered. No major differences between TDI and HDI elastomers were observed except in T_g values. The equilibrium swelling ratios in benzene were used along with equilibrium modulus data to calculate the polymer-solvent interaction parameter χ_1. This parameter was found to be independent of crosslinking density, but it increased with [U] and was slightly less of the HDI elastomers than for the TDI elastomers.

ACKNOWLEDGMENT

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RHEOLOGICAL TESTING OF ELASTOMERS AT LOW TEMPERATURES. PART II *

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The Low-Temperature Correlation Section of Subcommittee 27 of ASTM Committee E-1 on Methods of Testing, established March, 1951, has published reports of its work[1–4]. The present paper describes additional work performed as a result of the conclusions reached in the work on rheological testing[3]. It appeared that of the various test procedures studied, shear recovery (method I) offered some promise of an approach that would characterize an elastomer in respect to its rheological response at low temperature.

The basic theory is presented by Conant, Hall, and Lyons[5]. In brief, it is based on the demonstrated equivalence (measured by shear stressing) of creep and recovery at a given temperature and the extension of this concept into a continuous relationship between time, temperature, and rheological behavior.

The principle states that an elastomer under load at a certain temperature will attain a certain percentage of its equilibrium or ultimate strain at that temperature in a certain time; conversely, at this same temperature and time, it will recover the same percentage of its equilibrium strain when unloaded from a condition of equilibrium strain. It is to be noted that while the value of strain can be varied over a wide range, the percentages of creep or recovery will be nearly the same. The original paper demonstrates this equivalence for hevea, styrene-butadiene rubber (SBR), neoprene, butyl rubber, and butaprene formulations. Plotting creep (or recovery) as per cent against log time gives curves which characterize the various polymers.

All of the original data were obtained on specimens subjected to shear stresses. This method involves preparation of special test specimens consisting of a double sandwich in which the elastomer is vulcanized to separator plates, and a special stressing and strain-measuring apparatus. Correction for the

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Gough-Joule effect is inherent in the method of expressing deformation at a particular time as a percentage of the equilibrium strain or complete recovery at the given temperature.

Since the apparatus for testing in shear is somewhat complicated and not commonly available, the question presented itself of the possibility of measuring the same type of behavior under other forms of stress such as tension or torsion, apparatus for which is more widely available.

It was decided to investigate the problem by assigning to various collaborators certain subdivisions of the work, on a basis of their specialized equipment and experience.

The various phases of the work were performed by the following laboratories:

1. Shear creep and relaxation—Firestone Tire and Rubber Co., Akron, Ohio, under direction of F. S Conant.
2. Tensile creep and relaxation—United States Rubber Co., Passaic, N. J., under direction of W. E. Scoville, Jr.
3. Torsional creep and relaxation and stress decay—Naval Materials Laboratory, New York Naval Shipyard, Brooklyn, N. Y., under direction of C. K. Chatten and Max Hanok.
4. Correlation of results—Philadelphia Quartermaster Depot, U. S. Army, under direction of Ladislav Boor.

All compounds were prepared by Mr. Scoville, so that all laboratories were testing the same material. In addition, all test specimens except for those to be used in the shear test were prepared by Mr. Scoville, so that states of cure were uniform. The compounds used were the same hevea gum and SBR treadtype stocks as those used in the paper by Chatten[3].

EXPERIMENTAL PROCEDURE

The experimental procedure involved two phases for all forms of stressing. In the first phase, the equilibrium strain in shear, tension, and torsion and the equilibrium stress in tension was determined after an initial deflection of the specimen at 74° F, and after the subsequent reduction of the temperature to 20° F, 0° F, —20° F, —40° F, —50° F, —60° F, —70° F, and —80° F. The specimen was maintained in a deflected position throughout the entire procedure. This deflection of course increased with decrease in temperature for the creep determinations and was held constant for the stress determinations. Values were determined 10 min after deflecting the specimens at 74° F and 10 min after achieving thermal equilibrium at each of the succeeding lower test temperatures.

In the second phase of the experimental work, the creep and stress relaxation values were determined at intervals of 0,2. 0.5, 1, 2, 3, and 5 min after the initial specimen deflection at the lowest test temperature at which a required deflection could be produced. This was followed by determinations at the same time intervals at each of the succeeding higher temperatures used in the equilibrium determinations, up to and including 74° F. The specimens were conditioned for 10 min in the undeflected state at each of the test temperatures before applying a fixed load or a fixed strain for the determination of deflection or stress during the 5-min period. The deflected specimens were permitted to return to an assumed zero deflection by removing all of the deflecting force and then proceeding to the next higher temperature.

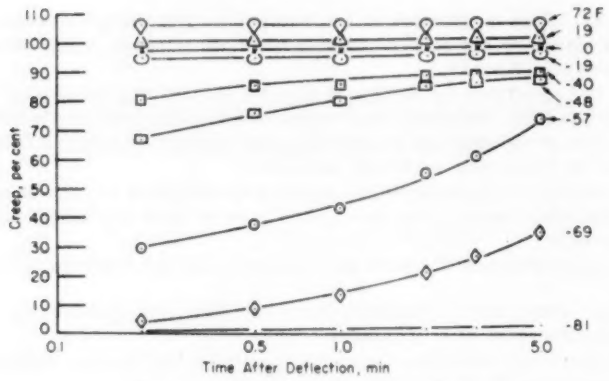


FIG. 1.—Torsional creep of hevea compound.

METHOD OF PLOTTING CONTINUOUS TIME-TEMPERATURE-RHEOLOGICAL PROPERTY CURVES

The creep and recovery data, obtained using the shear, torsional, and tensile methods, and the stress relaxation data, obtained using the tensile method, were plotted as families of curves of per cent rheological property as a function of log time, as shown in Figures 1 and 2. The ordinates in the creep and stress relaxation curves represent percentages of the equilibrium values determined at the indicated temperatures. The ordinates in the recovery curves represent percentages of the deformation recovered after unloading at each of the indicated temperatures.

The families of curves were then plotted as continuous functions of time, temperature, and rheological property in the manner described by Conant et al.[5] for shear creep and recovery, and by Tobolsky[6] for stress relaxation. In effect, the method consists of end-to-end joining of the families of curves in a given plot as those in Figures 1 and 2 into a continuous curve of the type shown in Figure 3 and 4, with the lower temperature portions of the curve appearing at the shorter log time intervals. The time scale of the composite curve, which consists of adjacent or overlapping 10^{-1} to 10-min periods, is made continuous

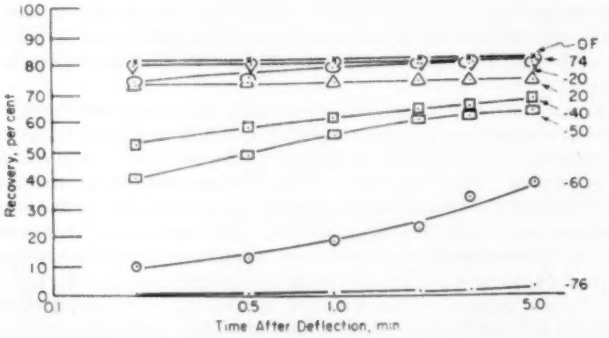


FIG. 2.—Torsional recovery of hevea compound.

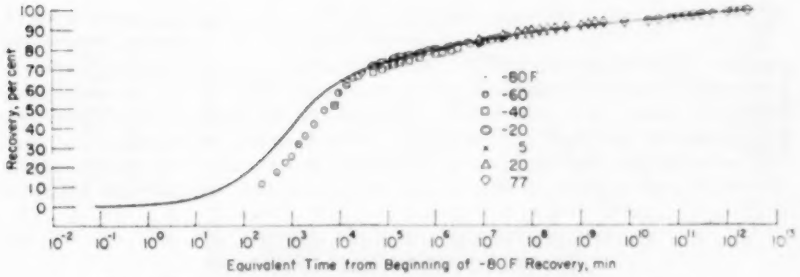


FIG. 3.—Time-temperature relationship from shear recovery of hevea compound.

by starting the time at which values are available at 10^{-1} min and naming each of the succeeding log cycles in increasing powers of 10.

The method of plotting the continous curves involves the assumption that if a continuous relationship exists, then discontinuities in the composite curves indicate the lack of data over a particular temperature range, while identical values determined at two succeeding temperatures indicate an identical rela-

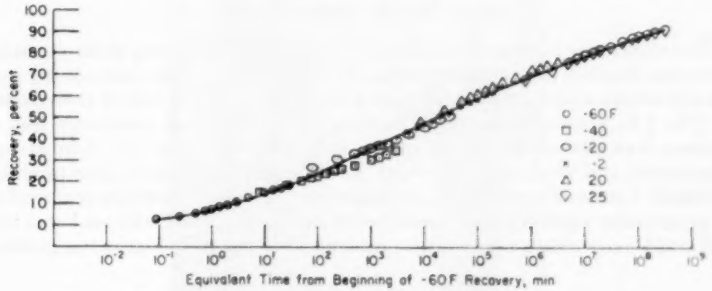


FIG. 4.—Time-temperature relationship from shear recovery of SBR compound.

tionship. Accordingly, in order to eliminate discontinuities in plotting the composite curves, one or more log time cycles were placed between plotted points, as required, and the curve was continued through these cycles. An example is seen in Figure 5 in which a time cycle was added in the time interval 10^6 to 10^7 min. On the other hand, the much more common occurrence was the appearance of nearly equal values at succeeding test temperatures. These

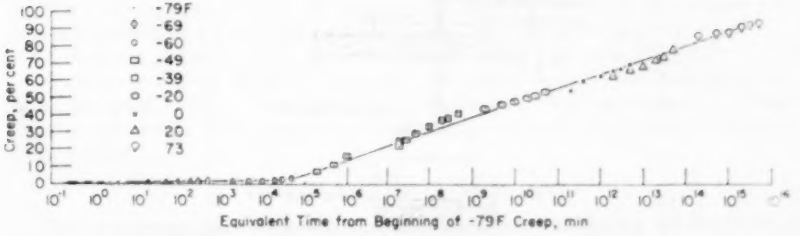


FIG. 5.—Time-temperature relationship from torsional creep of SBR compound.

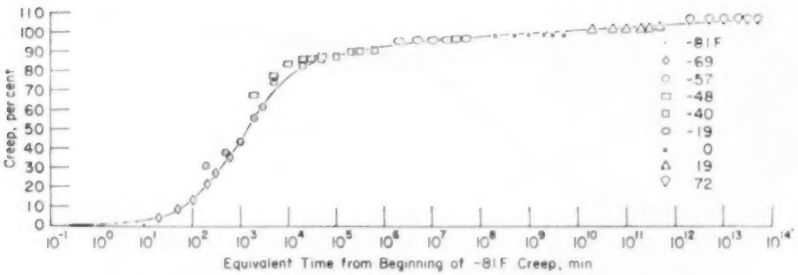


FIG. 6.—Time-temperature relationship from torsional creep of hevea compound.

points were overlapped by making the 1-min to 10-min cycle of one temperature identical with the 0.1-min to 1-min cycle of the next higher experimental temperature. In Figure 6, for example, the 2-min and 5-min values at −48° F are nearly coincidental with the 0.2-min and 0.5-min values obtained at −40° F.

DETAILS OF EACH PROCEDURE

SHEAR CREEP AND RECOVERY

The apparatus consisted essentially of a means of applying shear stress to a double sandwich-type specimen so that observations could be made of the specimen deformation as the test conditions were varied[1]. Each half of the sandwich was $\frac{1}{4}$ by $\frac{3}{8}$ in. cross-section and $3\frac{3}{4}$ in. long. In performing a recovery test, the specimen was allowed to remain under 80 lb (28.5 psi) load for 16 hr at room temperature and then cooled to —80° F while still under load, thus producing essentially a state of equilibrium deformation. The load was then removed and the progressive recovery was noted for 30 min, after which the load was reapplied and the specimen temperature was raised to the next higher temperature.

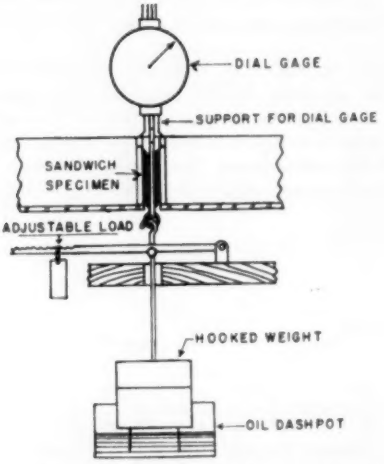
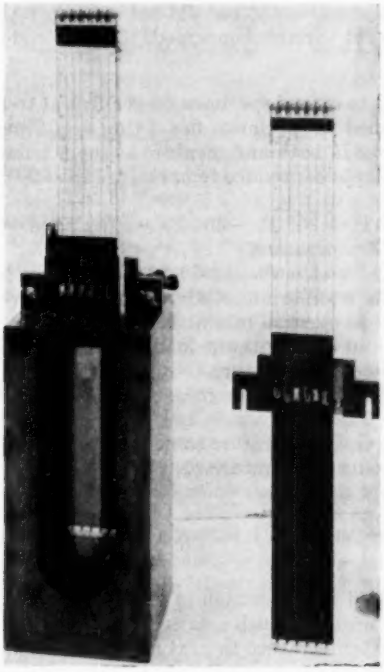


FIG. 7.—Diagram of shear creep and recovery apparatus.

Another recovery reading was obtained and then the test was repeated at still higher temperatures.

The shear specimens were adhered to steel end and center plates by a curing-type adhesive. Loxite 3000 manufactured by Firestone Tire and Rubber Co. was satisfactory for both hevea and SBR. Difficulties of clamping the specimen during the test were thus reduced to a minimum. The long, thin shape was chosen so that the deformation under load would approach pure shear. The principal difficulty associated with the use of a shear deformation is that of



Courtesy American Instrument Co.

FIG. 8.—Temperature-retraction apparatus.

specimen preparation. A special mold designed to hold the metal inserts is required, the inserts must be thoroughly cleaned and masked, the proper adhesive applied and a conditioning time before curing must be allowed.

A diagram of the essential parts of the apparatus is given in Figure 7.

Composite curves showing recovery from equilibrium shear deflection are given for hevea in Figure 3 and for SBR in Figure 4. Experience has shown that these curves would be duplicated by results showing percentage creep from zero deformation.

TENSILE CREEP AND RECOVERY

The apparatus used was the regular temperature-retraction (T-R) instrument used in ASTM Method D 1329 (1958 Book of ASTM Standards, Part 9,

p. 1423) and illustrated in Figure 8. The only modification was the use of an extra steel scale to measure retraction or extension under temperature and load changes. The glass flask used as a bath acted as a magnifying glass to aid in reading the 1-in. bench marks inscribed on the specimen. No difficulties were noted in reading. Sufficient load was applied to extend the T-50 specimens 50 per cent as noted by the upper graduated scale. Component weights of clamp wire and string were counter-balanced but not the specimen weight. Although the pulleys were not immersed in the bath, some frictional forces were present. They should, however, be nearly the same for creep as for recovery measurements. The stress load was noted but did not enter into the calculations since strain was the important variable concerned. The procedures were as follows:

Tensile creep.—

1. Determine load to extend specimen 50 per cent at room temperature.
2. With load applied to specimen, flex 8 times ±10 per cent, then rest 10 min under load. Place in bath and measure at room temperature.
3. With load still applied, reduce temperature to +20° F, hold 10 min and measure.
4. Continue to 0° F, −20° F, −40° F, −60° F, and −80° F, hold 10 min and measure at each temperature.
5. At end of −80° F test release load and remove from bath. Observations obtained represent the equilibrium strain at the respective temperatures.
6. Place specimen in oven 10 min at 158° F.
7. Place specimen in bath without load, depress temperature to −80° F, hold 10 min at stabilized temperature.
8. Add same load as in step 1 and measure extension at 0.2, 0.5, 1, 2, 3, and 5 min.
9. Remove load, raise temperature to next step, hold 10 min, repeat steps 8 and 9 until back to room temperature.

Tensile recovery.—

Run same tests as in steps 1 through 6. After oven aging continue as follows:

1. With load applied cool specimen in bath to −80° F; hold for 10 min.
2. Remove load, measure bench marks at 0.2, 1, 2, 3, and 5 min.
3. Add load, raise temperature to next step, hold 10 min.
4. Repeat steps 2 and 3 for each test temperature until back to room temperature.

Summary curves are shown in Figures 9, 10, and 11.

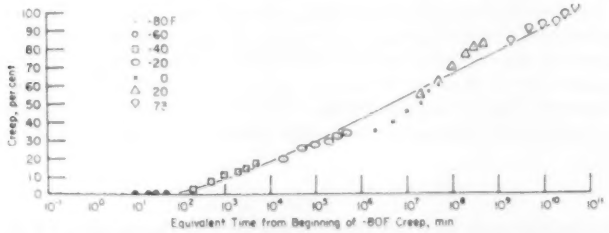


FIG. 9.—Time-temperature relationship from tensile creep of SBR compound.

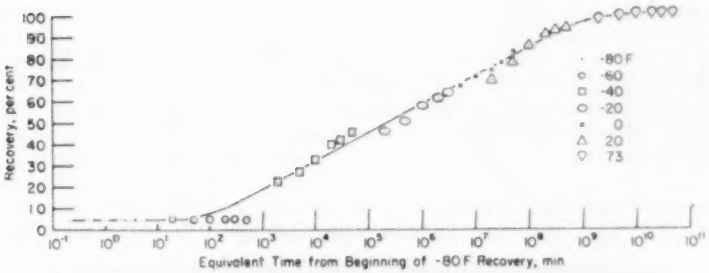


FIG. 10.—Time-temperature relationship from tensile recovery of SBR compound.

TORSIONAL CREEP AND RECOVERY

A Clash-Berg torsional tester[7] was used to determine both torisonal creep and torsional recovery (ASTM Method of Test for Stiffness Properties of Nonrigid Plastics as a Function of Temperature by Means of a Torsional Test (D 1043), 1958 Book of ASTM Standards, Part 9, p. 305). Rectahedral specimens, 2 in. long by ½ in. wide by a nominal slab thickness of 0.075 in. were placed individually in the 1-in. span between the jaws of this instrument, and the angular deflection was determined on the torsion head under a constant load and after removing the load, for the creep and recovery tests, respectively. The creep and recovery specimens were twisted through an angle obtained by suspending 5- or 15-g loads from each end of the load cord of the Clash-Berg apparatus for the hevea and SBR specimens, respectively. These loads resulted in deflection angles ranging between 200 and 275 deg at 74° F.

All tests were performed with the specimens immersed in an ethyl alcohol bath contained in a Dewar flask. Temperatures were controlled and maintained within ±2° F by the alternate addition of solid carbon dioxide to cool the bath, and the insertion of a heat resistant glass test tube containing hot water, for the heating cycle. Temperatures were determined with a type-K potentiometer using a copper-constantan thermocouple inserted in a thin, sealed glass tube immersed in the liquid bath.

In the torsional recovery tests, a constant load was first applied to both ends of the load cord at 74° F and the specimen flexed 10 times through 20 deg of arc on either side of the apparent rest point. The test temperature was then re-

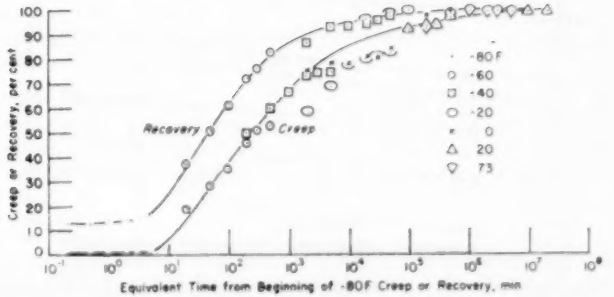


FIG. 11.—Time-temperature relationship from tensile creep and recovery of hevea compound.

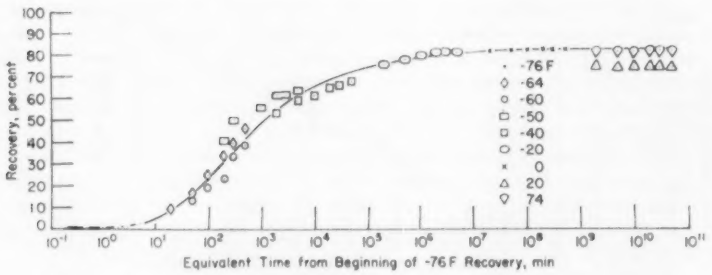


FIG. 12.—Time-temperature relationship from torsional recovery of hevea compound.

duced to the lowest experimental temperature, −76° F. After 10 min, the load was removed from both ends of the load cord and deflection angles were determined instantaneously, and after recovery times of 0.2, 0.5, 1, 2, 3, and 5 min. The torque load was then reapplied and the temperature was raised 10° F. This procedure was repeated at the succeeding experimental temperatures of −70, −60, −50, −40, −20, 0, and 74° F.

The experimental results are summarized in Figures 1, 2, 5, 6, 12, and 13. The curves were obtained by calculating the per cent creep as ratios of the creep (deflection angle) to the equilibrium values at equivalent temperatures, multiplied by 100. The recovery values were calculated as percentages of the maximum angle of twist at each temperature.

STRESS DECAY

A tensile stress relaxation apparatus[8] was used to determine the stress relaxation properties of the two experimental elastomer stocks in tension. The instrument and operational procedure have been described by Hanok et al.[9] A photograph of the apparatus is given in Figure 14 and of the specimen elongation jig in Figure 15. Essentially the instrument consists of a jig, which provides a means for maintaining a strain constant to within 0.1 per cent of the extended specimen length during measurements, and a load-measuring device which in this case was a Hunter Force Indicator. Two of these indicators were

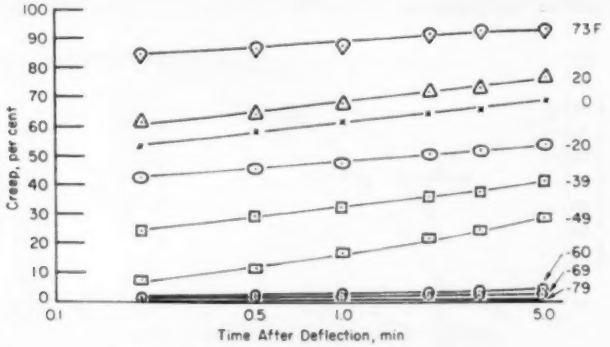


FIG. 13.—Torsional creep of SBR compound.

used according to the magnitude of the measured stress, one having a 500-g capactiy and the other a 5000-g capacity. The jig has fixed guides for extension in increments of 1 in. each. T-50 specimens (ASTM Method of Test for Physical State of Cure of Vulcanized Rubber (T-50 Test) (D 599), 1958 Book of ASTM Standards, Part 9, p. 1289), measuring 2 in. between tab ends by 0.075 in. wide in the constricted portion by a nominal 0.075 in. slab thickness, were used in the stress relaxation tests. They were given a 50 per cent deflection; that is, they were extended from 2 in. to 3 in.

Figures 16 and 17 show per cent stress relaxation plotted against log time for hevea and SBR compounds, respectively.

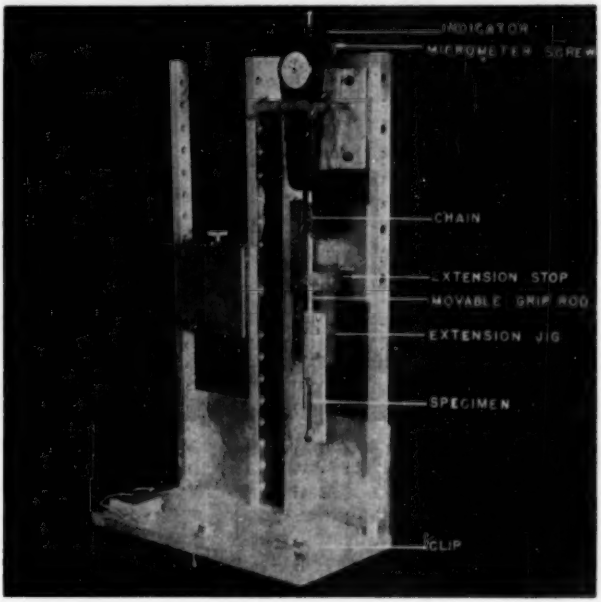


FIG. 14.—Tensile stress decay apparatus.

Figures 18 and 19 summarize the above data in a continuous curve of per cent stress versus log time.

A summary of the test results conducted by the three participating laboratories is shown in the following figures:

Shear, Recovery	Figs. 3 and 4
Tensile, Creep and Recovery	Figs. 9, 10, and 11
Torsion, Creep and Recovery	Figs. 1, 2, 5, 6, 12, and 13
Tensile, Stress Relaxation	Figs. 16, 17, 18, and 19

ANALYSIS

Since the shear stress procedure has undergone the most thorough study and validation, the other procedures were examined for their comparable ability to furnish the same information.

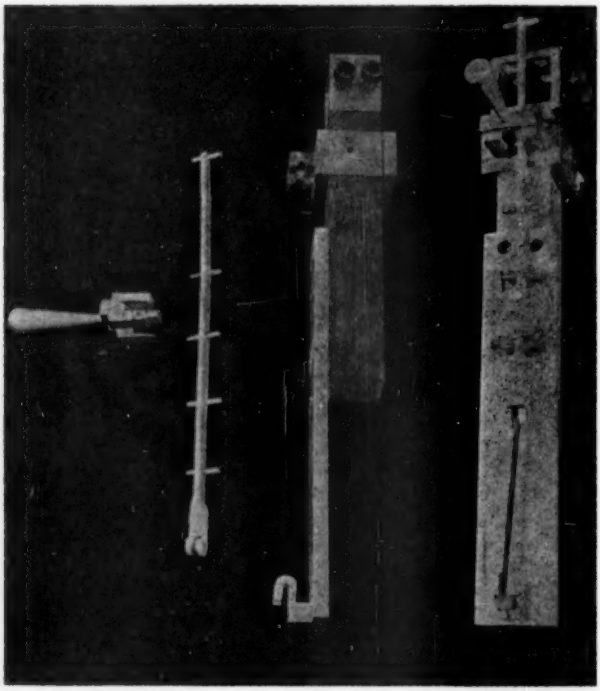


FIG. 15.—Specimen elongation jig—disassembled and assembled with specimen under strain.

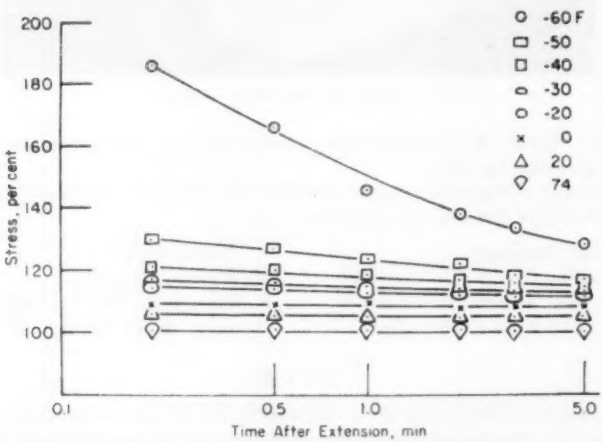


FIG. 16.—Tensile stress relaxation of hevea compound.

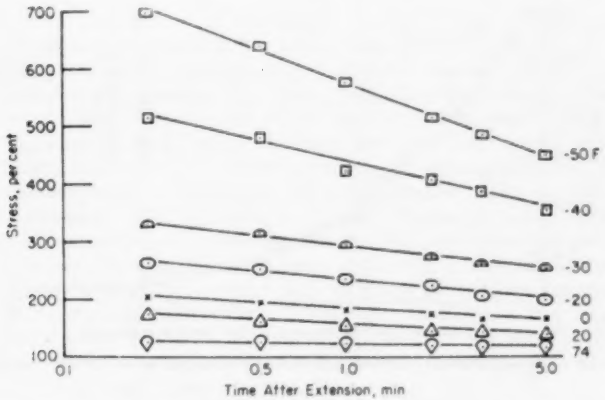


FIG. 17.—Tensile stress relaxation of SBR compound.

It is evident from the data in Figures 9, 10, and 11 that tensile creep from zero deformation did not follow the same deformation versus time path as did tensile recovery from equilibrium deformation. The reason for this lack of coincidence may be due to some inaccuracy in the test method.

Consider the characteristic modulus versus temperature curve for polymers shown in Figure 20. The experimental sigmoidal curves in Figures 6 and 12 show that the regions of glassy, leathery, and rubbery viscoelastic behavior were included in the experiments. The curves appear as inverse functions of the modulus of Figure 20. The stress relaxation curve in Figure 18 shows a similar resemblance to the characteristic modulus-temperature curve, but with the glassy region of the curve missing. The measurements were made only down to $-60°$ F which appears to be the beginning of the glassy transition region.

The continuous curves shown representing time-temperature relationships can be represented by empirical equation of forms differing from those in Reference 5. For example, the curve in Figure 13 is expressed by the following equation:

$$Y = AB^{C \log t}$$

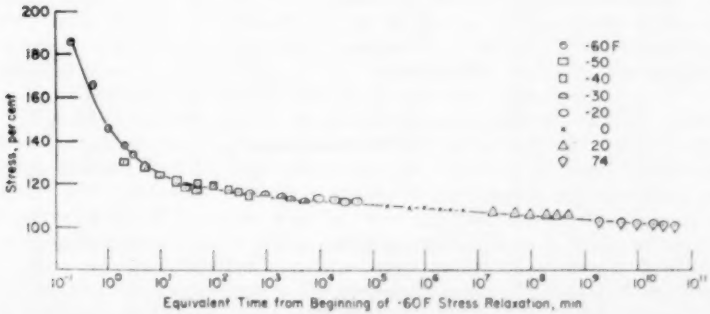


FIG. 18.—Time-temperature relationship from tensile stress relaxation of hevea compound.

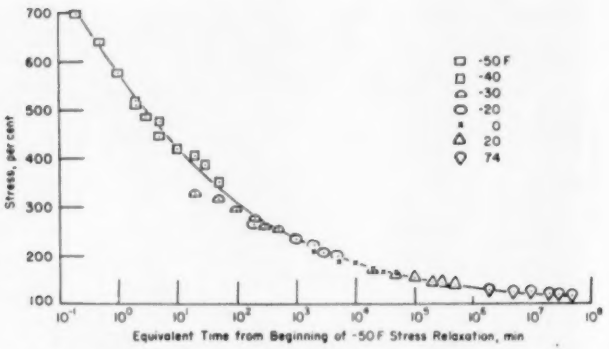


FIG. 19.—Time-temperature relationship from tensile stress relaxation of SBR compound.

where:

Y = per cent creep or recovery,
t = time, and
A, B, and C are arbitrary constants.

In this case $A = 99.13$, $B = 0.002324$, $C = 0.4687$.

The methods and instruments for the torsional creep and recovery and for the tensile stress relaxation determinations all showed deficiencies of varying degrees. One of the less significant types of deficiencies was a direct result of the normal stiffening of the elastomer specimens at the lower experimental temperatures. This produced errors in the assumed return of the specimens, especially the SBR specimens, to zero deflection after removing the deflecting load during the torsional creep tests. The elastomer stiffening also prevented the manual extension of the specimens to the required 50 per cent for the tensile stress relaxation tests at temperatures below $-60°$ F and $-50°$ F for hevea and SBR, respectively. Another deficiency was a consequence of the time-consuming manipulations involved in using the tensile stress relaxation apparatus, which caused some difficulty in determining the 0.2- and 0.5-min readings of

FIG. 20.—Characteristic temperature-modulus curve for polymers.

stress. The significance of this defect was minimized by the method of calculating per cent stress as a function of the equilibrium stress.

Much more significant deficiencies in the torsional recovery method, using the Clash-Berg apparatus, involved mechanical difficulties in achieving the required simultaneous removal of the load from both ends of the load cord at the beginning of each 5-min recovery period. This caused inaccuracies in determining the exact time of load removal, the entanglement of the load cord, an imbalance in the torsion head, and a disturbance in the equilibrium position of the specimen. The significance of these deficiencies, reflected in the data of Figure 12 was sufficient to warrant discontinuation of the test and to conclude that the Clash-Berg torsional stiffness apparatus is not suitable for the determination of torsional recovery of elastomers by the method described herein.

The incidence of values above 100 per cent in Figure 6 may be attributed to variable frictional effects in the torsion head of the Clash-Berg apparatus. The scatter of the data in Figure 12 may be due to disturbances in the equilibrium positions of the specimens during operation.

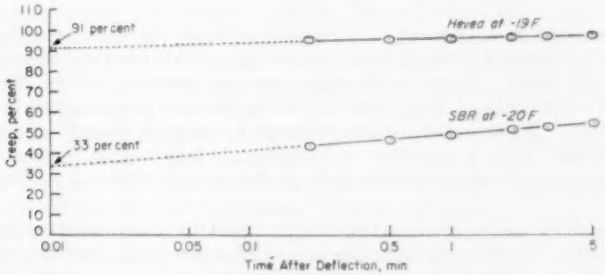


FIG. 21.—Torsional creep of hevea and SBR compounds extrapolated to near-instantaneous response.

DISCUSSION

The Conant type of plot which uses log time as abscissa is one way of summarizing the interaction between creep or relaxation, temperature, and time. For instance, it can be seen from Figure 4 that SBR at −60° F takes about 10^8 min (70,000 days, 191.78 yr) to attain 90 per cent of its equilibrium creep or recovery. Of more practical interest to rubber technologists is the relative behavior at shorter time intervals, such as 0.6 to 60 sec. The concept described supplies a means of arriving at such quantitative values by extrapolating the creep or recovery values obtained to shorter time intercepts.

Figure 21 shows torsional creep of hevea and SBR at −20° F. Extrapolation of these curves to the intercepts of 0.1 min (6 sec) and 0.01 min (0.6 sec) gives values reflecting degree of creep (or recovery) at these short intervals. From such extrapolated values can be constructed a set of curves such as Figures 22 and 23 in which creep (or recovery) can be estimated directly against temperature for the three (or as many as are significant) orders of time.

The validity of such extrapolation may well be questioned. Neglecting for the moment errors inherent in the mechanism used (frictional effects, exactness of readings), the 1-min value is an observed value, the 0.1-min (6 sec) is extrapolated from the first actual reading (12 sec). The most questionable value

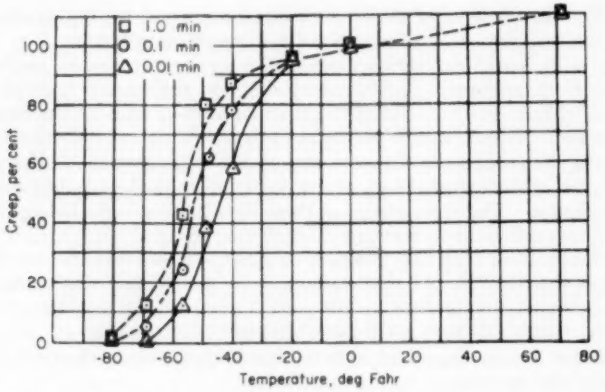


FIG. 22.—Summary of torsional creep versus temperature for hevea compound.

is that for 0.01 min (0.6 sec). Observed plots of log time versus creep (or recovery) are usually straight lines (Figure 21), within the time region in which readings are taken. Some of the single curves, however, will be concave upward and some concave downward depending on their position within the composite curve. Their extrapolation through a complete decade of time (from 0.1 min to 0.01 min) is a matter of judgment. Refinements in apparatus and procedures may throw additional light on the practicability of such extrapolations.

The authors know of no laboratory method to prove whether or not the values derived by this extrapolation are valid or accurate, and the idea is presented only as a basis for further experimental work. It might serve as a fingerprint method of characterizing the low-temperature response of elastomers, similar in a way to hardenability curves of ferrous alloys.

Roth[11] describes hardness measurements at a series of low temperatures on a Wallace meter. He obtained composite creep curves by matching segments of compliance versus log time curves, obtained at different temperatures. The

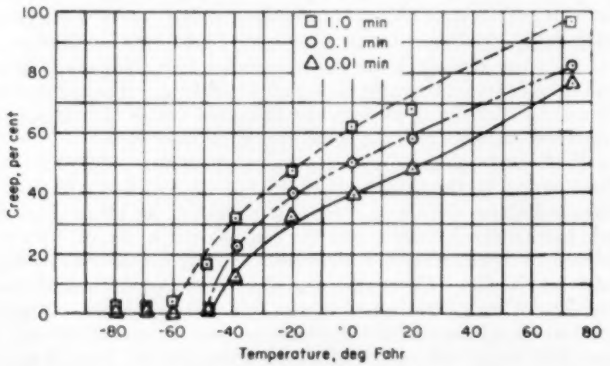


FIG. 23.—Summary of torsional creep versus temperature of SBR compound.

data were normalized to correct for Joule effect by multiplying compliance by absolute temperature rather than by obtaining percentages of equilibrium deflection as was done in the present work. His method of analysis also permits long-time creep properties to be evaluated from relatively short-time tests and indicates that deflection of a rubber-like material under load is a unique function of time and temperature.

Payne[12] has shown how curve-fitting of the nature used in the present work can be used to obtain a T_s value which characterizes a particular polymer not only for various types of deformation but also for dielectric measurements. His T_s is a reference temperature to which all of the experimental data are reduced in plotting continuous curves.

The possibility of using resistance to indentation, which is a form of compressive loading, for developing a basic pattern of rheological response is indicated by the time-indention curves (Figures 5, 6, 7, of Labbe's summary of hardness tests[2]. Eight different hardness testers were compared, and their response, in depth of indentation (or scale reading), is shown for time up to 100 sec).

Bearing in mind that the instruments differed in the mechanism of load application (spring versus dead weight) and that the unit stress at the indentation point varied in the instruments, the general pattern of response was similar to the observed creep behavior in shear, tension, and torsion, namely,

1. A region of almost instantaneous elastic response and high indentation around room temperature.
2. A region of slow response, within the 100-sec time—for example, -40 to $-60°$ F for natural rubber gum stock.
3. A region of extremely slow response ($-80°$ F or lower) where equilibrium indentation would be attained in a matter of hours or days.

Since Labbe was concerned only with hardness effects, no attempt was made to observe the rate of recovery after removal of major load. It is possible that these rates of recovery would be consistent with the creep and recovery phenomena as observed in shear, tension, and torsion.

CONCLUSIONS

The curves in Figures 3, 4, 5, 6, 9, 10, 11, 12, 18, and 19 show the existence of continuous relationships between time, temperature, and the rheological properties of shear creep, shear recovery, torsional creep, torsional recovery, and tensile stress relaxation. There is excellent agreement between the torsional creep and recovery curves and the shear creep and recovery curves, and there is a significant resemblance between these and the tensile creep and recovery curves in Figures 9, 10, and 11. The characteristic sigmoid-shape curve for hevea is especially noticeable for the torsional, shear, and tensile methods. It is noteworthy that an inflection point appears over the narrow range of 42 ± 2 per cent creep in all of the creep curves for hevea; and that the region of greatest rate of change of the creep occurs over two logarithmic time cycles. The inflection point occurs at a temperature of approximately $-60°$ F. This appears to indicate a time-temperature-creep point above which the crude rubber behaves as an elastomer and below which it behaves as a nonserviceable, highly viscous material. Bennett et al.[10] have noted that the lower limits of serviceability of elastomers are actually about 15 to 30 degrees above their glass transition temperatures. The glass transition temperature of natural rubber was placed at $-97.6°$ F.

The relationship between stress relaxation and creep or recovery is not clearly demonstrated by the experimental curves. It should be noted that the stress relaxation data, Figures 18 and 19, were not determined over the full range of temperatures covered by the creep and recovery curves. It appears from the continuous nature of the curves, however, that both the creep-recovery curves and the stress relaxation curves may be used as independent indexes of elastomeric behavior.

Despite the scatter of the data for torsional recovery, Figures 6 and 12 show an equivalence between torsional creep from zero deformation and torsional recovery from equilibrium deformation, which is similar to the equivalence between shear creep and shear recovery[5]. The tensile method does not demonstrate this equivalence.

RECOMMENDATIONS

Since the pattern of rheological response of elastomers at low temperatures appears to be essentially the same regardless of the manner of stressing (shear, tension, torsion), it would be reasonable to expect the same response in compression, and some work in this direction has been described by Roth[11].

Compression (or indentation) testing has recently undergone considerable refinement, and instruments are available (Wallace, Material Laboratory Indentometer, Pusey and Jones[2]) which embody improvements to minimize frictional and thermal expansion effects, and which will measure with great precision the changes in indentation with various loads over a wide temperature range.

It is recommended that a study be made, utilizing indentation at various loads (major and minor) over the usual range of temperatures, to explore the possibility of simpler instrumentation to establish the basic curve of rheological response.

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SUMMARY

Results are given from a cooperative study to determine the extent to which certain superposition principles are applicable to analysis of different types of deformation of elastomeric materials. Briefly, these principles are: (1) recovery rate from an equilibrium deformation after removal of a given load is equivalent to the creep rate from zero deformation upon application of that load and, (2) creep, recovery, or stress relaxation curves obtained at different temperatures can be pieced together into a continuous curve of time *versus* deformation or stress. Both principles are predicated on the use of an essentially equilibrium deformation or stress as a base from which the percentage change with time is calculated.

The first of the above principles was demonstrated for both torsional and

shear deformations, but not for tensile deformations, possibly because of some inaccuracy in the test method. The second principle was demonstrated for shear creep, shear recovery, torsional creep, torsional recovery, and tensile stress relaxation. Applications of this method of analysis are given to show how the rheological behavior of an elastomer at a given temperature may be predicted for very short or for very long periods of creep, recovery, or stress relaxation from measurements made at a series of temperatures.

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DETERMINATION OF COPOLYMER COMPOSITION BY COMBUSTION ANALYSIS FOR CARBON AND HYDROGEN *

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INTRODUCTION

Elemental analysis is probably the most fundamental and unambiguous method of determining the composition of many polymers. When the polymer is a copolymer of two components differing appreciably in carbon-hydrogen ratios, the analyses for carbon and hydrogen by combustion may be used to determine the relative amounts of the two components. It is perhaps the only method that is completely free from possible structural effects. The present work describes in detail the method of combustion analysis used at the National Bureau of Standards to determine the ratio of bound styrene to butadiene in different samples of styrene-butadiene synthetic rubber (SBR, formerly called GR-S). Little modification would be required to apply the method to other hydrocarbon copolymers. Further study of each system would be required to determine its applicability to copolymers containing elements that might cause interference with the determinations of carbon and hydrogen.

References to carbon-hydrogen determinations on polymers in other laboratories are relatively rare. Kemp and Peters[1] in 1943 at the Bell Telephone Laboratories, in conjunction with their work on unsaturation as determined by iodine chloride addition, published some results of carbon and hydrogen determinations on styrene-butadiene copolymers and used them to make calculations of the bound styrene. No details of their procedure of measurement have been published. With the exception of this publication and two others[2, 3] which give results as a very minor adjunct to other work, we are not familiar with any other carbon and hydrogen determinations on polymers. Consequently, it has seemed desirable to describe in detail the practices employed at the National Bureau of Standards in such determinations.

Carbon and hydrogen determinations have been made with high precision at NBS since about 1929. References to the earlier work are given in a paper by Wagman and Rossini[4]. The method was employed to give information regarding the composition of purified natural rubber by Smith, Saylor, and Wing[5, 6]. The present work was initiated in 1944 as a part of the government synthetic rubber program[7, 8]. Slight modifications and improvements in the method were made over the following years until about 1951. Since then the procedure has remained essentially unchanged.

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The procedure is too time consuming and tedious to be applied to routine determinations on samples of only casual interest. It likewise calls for so much care in order to make the determinations with the requisite precision that it cannot be recommended for general use. However, it is well adapted to use in measuring the copolymer composition of reference samples intended for standards in developing new procedures. For examples, the standards may be used to determine the relationship between the composition and some other property that can be easily measured. In the present instance one of the chief applications of the method was to measure the bound styrene content of samples to be used in determining the relationship of refractive index to the composition of SBR (GR-S) polymers[9–11]. Many of these samples were also used in studies of heats of combustion[12], specific heats, and other thermal properties[13–15] at NBS. The results of the analyses of these samples have already been reported in the published papers.

METHODS OF CALCULATION

CALCULATION FOR A PURE COPOLYMER

In a copolymer of two hydrocarbon monomers, one of composition C_jH_k and the other of composition C_pH_q, let the percentage of the weight arising from the first monomer be denoted by X, and the carbon-hydrogen ratio of the polymer be denoted by R. Analysis then requires the calculation of values of X from observed values of R. By expressing both of these quantities one can derive the following equation:

$$\frac{X}{100} = \left[\frac{jA_C}{jA_C + kA_H} - \frac{pA_C}{pA_C + qA_H}\right]^{-1}\left[\frac{qA_H}{pA_C + qA_H} - \frac{1}{R+1}\right] \quad (1)$$

where A_C and A_H, the atomic weights of carbon and hydrogen, are 12.011 and 1.0080, respectively[16].

If the equation is applied to a copolymer of styrene (C_8H_8) and butadiene (C_4H_6), one has $j = 8$, $k = 8$, $p = 4$, and $q = 6$. The equation then becomes

$$X = 29.0831[11.1809 - 100/(R+1)] \quad (2)$$

For the purpose of calculation of theoretical values, the constants in this equation are given to one more significant figure than would be justified by the probable uncertainty in the accepted atomic weights.

Table I shows the values given by this equation for butadiene, styrene, and

TABLE I

THEORETICAL CARBON–HYDROGEN RATIOS

Butadiene, C_4H_6		7.9438
Butadiene: %	Styrene: %	
80	20	8.5299
79	21	8.5613
78	22	8.5928
77	23	8.6245
76	24	8.6565
75	25	8.6887
Styrene, C_8H_8		11.9157

several of their copolymers. Differentiation of the equation shows that each per cent change in styrene content produces a change in carbon-hydrogen ratio ranging from about 0.0275 for polymers of low styrene content to about 0.057 for polymers of high styrene content. In the range of normal SBR, containing about 24-per cent styrene, the value is about 0.032. The relation has been presented in graphical form by Kemp and Peters[1].

It is clear that the carbon-hydrogen ratio must be measured with considerable accuracy if an accuracy of a few hundredths of a per cent in styrene content is to be obtained. However, there need be no concern for the uncertainty introduced into the calculations by uncertainty in the accepted values of the atomic weights of carbon and hydrogen, since it is of the order of magnitude of hundredths of a per cent styrene.

CORRECTIONS FOR MINOR CONSTITUENTS

The discussion thus far has related to an ideal copolymer containing only material arising from the two hydrocarbon monomers. Actual copolymers, especially those made by emulsion polymerization, contain minor constituents. Some of the minor constituents are readily removable by extraction or by solution and precipitation of the polymer. Soap, fatty acid, and stabilizer should normally be removed in this manner so that corrections for their carbon-hydrogen ratios need not be made. The effort spent on such purification is well-justified in terms of increased accuracy. Table II shows the carbon-hydrogen ratios of some of these constituents. Special pains should be taken to free the polymer from those minor constituents with carbon-hydrogen ratios differing widely from that of the copolymer. Equal attention should be given to the removal of traces of liquids used in purification.

TABLE II

THEORETICAL CARBON–HYDROGEN RATIOS

Dodecyl mercaptan $C_{12}H_{25}SH$	5.4995
Phenyl-naphthylamine $(C_6H_5)NH(C_{10}H_7)$	14.6654
Stearic acid $CH_3(CH_2)_{16}COOH$	5.9578
Sodium stearate $CH_3(CH_2)_{16}COONa$	6.1281
Benzene C_6H_6	11.9157
Methanol CH_3OH	2.9789

It should be pointed out that minor constituents containing neither carbon nor hydrogen can be tolerated, since their presence does not affect the carbon-hydrogen ratio. Of course, elements that can cause interference with the actual experimental measurements of carbon and hydrogen should be avoided. Likewise, the addition of oxygen to the polymer at room temperatures may be presumed to be without effect, since there is no evidence of evolution of carbon dioxide or water by the polymer during such oxidation. These facts are the fundamental reason why it is desirable to base calculations of this sort on the carbon-hydrogen ratio rather than the per cent carbon or the per cent hydrogen in the sample. As would be expected, experimental accuracy is found to be much better when this is done.

According to modern ideas of polymerization[17], the mercaptan used as modifier in the emulsion polymerization of SBR is split into a free radical and a hydrogen atom, one of which initiates and the other terminates a polymer chain. Consequently, the mercaptan is chemically bound in the polymer and cannot be removed by the methods employed to remove the other minor constituents.

It has been the practice at NBS to measure the amount of sulfur in the purified polymer and to calculate from it the amounts of bound mercaptan. The presence of the sulfur is, of course, of no consequence, as shown by direct experiments mentioned later, but the carbon-hydrogen ratio of the mercaptan assumed to be bound in the polymer is even lower than that of polybutadiene, as may be noted in Table II. The carbon content and the hydrogen content of the portion of the sample consisting of bound mercaptan are subtracted from the directly-observed carbon and hydrogen contents in the calculation of the carbon-hydrogen ratio of the pure copolymer.

The modifier commonly used in butadiene-styrene emulsion polymerizations at 50° C is a mixture of mercaptans, with the major constituent *n*-dodecyl mercaptan. Next in importance in the mixture are tetradecyl and decyl mercaptans. It has been found sufficiently accurate for present purposes to make calculations as if the mixture consisted entirely of dodecyl mercaptan. For low temperature (i.e., 5° C) polymerizations the modifier most commonly used is Sulfole B-8. This is chiefly tertiary dodecyl mercaptan, which, of course, has the same elementary composition as the *n*-dodecyl mercaptan.

APPARATUS AND PROCEDURE

APPARATUS

The apparatus used for the combustion was developed from that used in the analysis of benzoic acid by Wagman and Rossini[4]. In the present work the polymer is burned in a stream of oxygen in a quartz combustion tube. That portion of the tube which is in the combustion furnace is packed with cupric oxide wire. The oxygen is first freed of combustible impurities, carbon dioxide, and water by passage through a combustion tube and a train of Ascarite, magnesium perchlorate, and phosphorus pentoxide before it comes into contact with the polymer.

Each sample is placed in a small Pyrex test tube capped with platinum gauze. This arrangement controls the rate of combustion much more satisfactorily than is possible with a platinum boat. This control is especially important when the styrene content of the copolymer is low.

The furnace is a common commercial type with fixed and movable electrical heating units.

The products of combustion are collected in absorption tubes of a design[18] differing from the U-type formerly employed. One of the tubes is packed with magnesium perchlorate and phosphorus pentoxide to absorb the water formed in the combustion. The other tube is packed with Ascarite to absorb carbon dioxide, and with magnesium perchlorate and phosphorus pentoxide to retain water liberated by the reaction of the carbon dioxide with the Ascarite. Weighings are made to hundredths of a milligram on a high-precision analytical balance.

PREPARATION OF POLYMER SAMPLE

Purification of the sample of polymer is of the highest importance, as already mentioned. The purification procedure now employed was developed in the course of the present work. The later stages of the development and the application to the samples here described were carried out by Max Tryon. The polymer is first dissolved in benzene and the solution is added dropwise to well-stirred methyl alcohol to coagulate the polymer. The coagulated polymer is then redissolved in benzene. The solution and precipitation processes are

carried out three times. This procedure serves to eliminate fatty acids and their salts, stabilizer, and some of the low-molecular-weight polymer. The solution of polymer in benzene is finally frozen by the use of solid carbon dioxide. The refrigerant is then removed and the benzene is sublimed from the system at a low pressure produced by a vacuum pump. This process yields a spongy mass of polymer, which is stored at a low temperature in a vacuum desiccator over magnesium perchlorate until it is cut up for individual analyses. Any possible oxidation during storage should be at a minimum under these conditions.

PROCEDURE

A sample is removed from the desiccator and cut into small pieces. Eight or more Pyrex test tubes (75-mm long, 12-mm in diam) are cleaned, dried, and weighed. All of the test tubes are filled at the same time with samples weighing between 0.5 and 2 g. The filled test tubes are dried in the vacuum desiccator for 2 hr to remove moisture picked up during the cutting and filling. They are then weighed. Samples are prepared at the same time for determination of sulfur and oxygen.

When a determination is begun the preheater and combustion coils are turned on and the flow of oxygen is adjusted to 250-ml per min. When the fixed unit of the furnace has reached its operating temperature of 800° C, a filled test tube is capped with a piece of platinum gauze, placed on a support of platinum gauze, and is inserted, capped end first, into the combustion tube until the capped end is 6 cm from the end of the fixed heating unit. The combustion tube is swept out with oxygen for 20 min and then the weighed absorption tubes are attached. The absorption tubes are flushed with hydrogen prior to each weighing in order to decrease the magnitude of the correction made for the increase in volume of the solid phase, with resulting decrease in the volume of the gas phase, during the run. Each tube is weighed against a counterpoise of a similar closed absorption tube filled with hydrogen. The movable heating unit is then turned on and pushed forward over the sample until it is 5 cm from the fixed unit. An asbestos pad is inserted between the units.

The temperature of the movable unit is raised rapidly to 300° C and then slowly to 400° C. If the latter temperature is approached too rapidly or if it is exceeded, the polymer sample usually decomposes rapidly, flashes, and burns with violence. Rapid decomposition is indicated by oscillation of the mercury in the flowmeter. If the temperature of 400° C is approached too slowly, carbon forms in the test tube and can be oxidized only at a very slow rate. When conditions are satisfactory, combustion is complete in about 1½ hr. With proper control of temperature some samples are completely decomposed without ignition. Others flash lightly and afterward burn with a small flame at the mouth of the test tube. Under the best conditions no free carbon appears.

After the initial combustion the temperature is slowly increased to 600° C. This is sufficiently high for complete pyrolysis and not high enough to cause softening of the Pyrex test tube. Under normal conditions of slow combustion there is no need to cool the trap that condenses water. Five hours after the absorbers are attached the flow of oxygen is increased to 400 ml per min. Hot water is placed around the water trap and is removed. This operation is repeated several times until the condensed water has disappeared. One hour later the asbestos pad is removed and the movable heating unit is pushed against the fixed unit. The absorbers remain attached for 7 hr. They are then re-

moved and flushed with hydrogen. After grease is dissolved from the spherical glass joints with ether, the absorber and counterpoise are placed in the balance case. They are weighed on the following morning.

The amounts of sulfur in the polymers studied were too low to affect significantly single determinations of carbon and hydrogen, as shown by check experiments utilizing mixtures of benzoic acid with a few tenths of a per cent of sulfur. However, when a combustion tube has been used for a long period, it was found that traces of sulfuric acid might collect in the trap that condenses water. In this case, water was retained and the amount of hydrogen found in an analysis was lower than that in the polymer. When the presence of sulfuric acid was suspected, the combustion tube was cleaned and repacked.

TABLE III

ANALYSIS OF BENZOIC ACID

		Wagman and Rossini	Madorsky	Cheek
Carbon	%	68.8367	68.836	68.8357
Theoretical	%	68.8450	68.8450	68.8450
Difference	%	−0.0083	−0.009	−0.0093
Standard deviation	%	.0013	.0020	.00047
Hydrogen	%	4.95461	4.9542	4.9520
Theoretical	%	4.95230	4.95230	4.95230
Difference	%	+0.00231	+0.0019	−0.0030
Standard deviation	%	.0010	.0013	.00045
C/H ratio		13.8931	13.8945	13.9006
Theoretical		13.9016	13.9016	13.9016
Difference		−0.0085	−0.0071	−0.0010
Standard deviation			.0048	00.14

SUBSIDIARY MEASUREMENTS

In the determination of sulfur, a 0.2-g sample of the purified polymer is decomposed by the Carius method[19, 20]. The sulfur is precipitated and weighed as barium sulfate by the conventional microtechnique. The Parr bomb method did not prove to be as reproducible as the Carius method. The results of the sulfur determination are used to calculate the bound mercaptan content of the copolymer, as discussed in an earlier section.

The amount of oxygen in the polymer is measured by the modified Unterzaucher method developed by Walton, McCulloch, and Smith[21]. The oxygen is converted to carbon monoxide, which is then measured by the use of the NBS colorimetric indicating gel. The ash is determined by simply weighing the sample after the combustion analysis for carbon and hydrogen. The results of the determinations of oxygen and ash are of used in estimating how well the polymer has been purified but do not enter directly into the calculations.

RESULTS FOR COMPOUNDS OF KNOWN COMPOSITION

BENZOIC ACID

In order to obtain information on the precision and accuracy of the method and to make comparisons with the work of other observers, a series of combustions of purified benzoic acid was made. The benzoic acid used was from a lot of NBS Standard Sample 39f.

TABLE IV

ANALYSIS OF POLYBUTADIENE

	NE-1	GL-657	36	38	MS-1045
	%	%	%	%	%
Carbon	88.656	88.656	88.554	88.486	88.474
Hydrogen	11.1873	11.1795	11.171	11.166	11.1600
Sulfur	0.112	0.072	0.098	0.109	0.083
Oxygen	.145	.145	.16	.145	.12
Ash	.00	.097	.099	.100	.34
Total	100.1003	100.1495	100.082	100.006	100.177

Table III shows a comparison of values obtained by Wagman and Rossini[4] with those obtained in the first (Madorsky, 1944), and second (Cheek, 1948) stages of development of the present procedure.

It will be noted that the percentage of hydrogen found agrees with the theoretical value within the error of determination but that the percentage of carbon is significantly lower than the theoretical value in all cases. The cause of this discrepancy is not known.

POLYBUTADIENE

In order to obtain further information on the precision and accuracy of the method measurements were made on several samples of polybutadiene. These samples of known composition, of course, possessed a structure nearly the same as the copolymers in which the chief interest was centered. The samples were purified in the manner already described. The results of the analyses are given in Table IV. The carbon and hydrogen results are the mean values of five determinations; the sulfur results are the mean of three. Some of these results were utilized in the thermodynamic studies already published[12, 13].

The totals in most cases are about 0.1 per cent more than 100 per cent. The reason for this is not apparent; it is possible that the mineral contaminants responsible for the ash contain some sulfur or oxygen (perhaps as SO_4 or CO_3) which has already been accounted for in the direct analysis for these elements. The oxygen content varies relatively little. The sulfur content depends on the amount of mercaptan used in polymerization and on other polymerization conditions. The ash content, likewise, depends on the conditions of polymerization and purification. It is notably higher for polymer MS-1045, which is the only one shown polymerized at 5° C, where the recipe would be expected to yield a much higher ash content. The sulfur and oxygen are slightly lower than in the others, so that the higher ash does not produce much increase in the total.

TABLE V

TYPICAL CALCULATION OF CORRECTED CARBON–HYDROGEN RATIO
(NE-1 polybutadiene)

Determination	C	C′ = (C-0.503)	H	H′ = (H-0.0915)	R′ = C′/H′
	%	%	%	%	
1	88.665	88.162	11.1845	11.0930	7.9475
2	88.663	88.160	11.1919	11.1004	7.9421
3	88.668	88.165	11.1913	11.0998	7.9429
4	88.701	88.198	11.1931	11.1016	7.9446
5	88.583	88.080	11.1758	11.0843	7.9464
Mean					7.9447

Table V shows a typical calculation of the correction of measured values of carbon and hydrogen to eliminate the effect of the bound mercaptan. The sample NE-1 polybutadiene—as noted in Table IV—was found to contain 0.112 per cent sulfur corresponding to 0.707 per cent bound mercaptan. This in turn was responsible for 0.503 per cent carbon and 0.0915 per cent hydrogen. These are substracted from the observed values, and the carbon-hydrogen ratio of the pure polymer is calculated. The mean value of this ratio R' and those for four other polybutadienes are given in Table VI. The comparison of values shows excellent agreement with the value calculated from the composition—the mean value of all differing by only one in the fifth significant figure. The individual differences from the theoretical value are shown in the last column for comparison with the standard deviations, as calculated from the separate determinations of R' for each sample. In all but one case the error is less than one standard deviation. From statistical theory this situation should occur two-thirds of the time if there are no systematic errors. We conclude that systematic errors are not significant here.

TABLE VI

PRECISION AND ACCURACY OF CORRECTED CARBON–HYDROGEN RATIOS (POLYBUTADIENES)

	R'	Standard deviation	Difference from theoretical
Theoretical	7.9438		
NE-1	7.9447	0.0010	+0.0009
GL-657	7.9432	.0009	−.0006
Sample 36	7.9446	.0014	+.0008
Sample 38	7.9442	.0013	+.0004
MS-1045 (5° polymer)	7.9426	.0010	−.0012
Mean	7.9439	.0011	.0008

Possible sources of systematic error, if found, would be incomplete extraction of minor constituents (other than bound mercaptan), the presence of residual solvent or precipitant following incomplete drying, and variations in the carbon and hydrogen contents of the bound mercaptan from those calculated for dodecyl mercaptan.

Both the errors and the standard deviations in four out of five cases are smaller than those previously given in Table III for benzoic acid. This is probably the result of small improvements in technique since 1948. We conclude that the accuracy and precision of the carbon-hydrogen determination are in no way impaired by the use of a well-purified polymer instead of a compound of low molecular weight.

The generally satisfactory nature of the values shown in Table VI for polybutadiene, where the composition is known, gives us confidence in the accuracy of similar values determined for copolymers of butadiene with styrene and other monomers, where there are no other satisfactory methods of determining the composition with equal precision.

PRECISION OF VALUES FOR COPOLYMERS

Table VII shows values of the standard deviation of the carbon-hydrogen ratio R' found for a number of styrene-butadiene copolymers differing in styrene content. The elemental analyses for most of these polymers are given in papers

on thermodynamic studies[12, 14, 15]. The values of standard deviation are essentially the same as those shown in Table VI for polybutadiene. No correlation with styrene content or temperature of polymerization is apparent. From the mean value (0.0010) of the standard deviation of R' one may calculate the standard deviation of X, the bound styrene content, using the values of the derivative of Equation (2) given in an earlier section. One obtains a standard deviation of 0.036 per cent bound styrene for polymers of low styrene content or 0.018 per cent for polymers of high styrene content. In the range of normal SBR, containing about 24 per cent styrene the value is 0.031.

TABLE VII

PRECISION OF VALUES FOR BUTADIENE–STYRENE COPOLYMERS

Designation	Styrene content	Standard deviation of R'
50° copolymers	%	
GL-658	8.58	0.0009
MS-1726	8.69	.0006
MS-1232	10.71	.0007
MS-1728	11.4	.0016
48-B	55.73	.0006
NE-6	83.67	.0012
5° copolymers		
X-454	8.58	.0010
X-478	22.61	.0011
GL-660	36.26	.0014
GL-661	53.09	.0010
Mean value		.0010

CONCLUDING REMARKS

The procedure described attains its accuracy and precision by the refinement and improvement of conventional simple operations over a periods of years. The trend in analysis recently is, of course, toward the use of rapid physical methods. In a great many instances these involve relative measurements requiring the initial establishment of reference materials with compositions determined by methods such as the one here described, which bases the numbers derived solely on readings of an analytical balance. In fact, as already mentioned, one of the principal applications of the present method has been in the establishment of the relation between refractive index and styrene content for SBR polymers so that refractive index measurements can be used in routine determinations of bound styrene content.

SYNOPSIS

A detailed description is given of the method of combustion analysis for carbon and hydrogen to determine the composition of a copolymer from its carbon-hydrogen ratio. The apparatus and procedures have been developed at the National Bureau of Standards over a period of years. The method has been applied chiefly to determine what fraction of a styrene-butadiene copolymer is derived from styrene. Minor ingredients are removed by extraction, with the exception of the bound mercaptan residue for which correction must be made. The amount of bound mercaptan residue is determined from measurements of the sulfur content of the copolymer by the Carius method. Meas-

urements are made of the oxygen content and the ash content, although these do not enter into the calculations. The standard deviation of a measurement of carbon-hydrogen ratio is approximately 0.0010 and is independent of styrene content. This corresponds to a standard deviation of about 0.036-per cent bound styrene for polymers of low styrene content and 0.018 per cent for polymers of high styrene content. The accuracy of the method is demonstrated by the fact that observations of carbon-hydrogen ratio for four out of five samples of polybutadiene differed by less than one standard deviation from the theoretical value.

ACKNOWLEDGMENTS

Contributions to the development of the method here described were made by a number of individuals whose assistance is gratefully acknowledged. Special mention should be made of the late W. H. Smith, who maintained a continuing interest in the problem for many years, and Max Tryon, who purified most of the samples. Others included R. D. Rossini, D. D. Wagman, W. W. Walton, F. W. McCulloch, and Conrad H. Cheek.

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THE ATTACK OF OZONE ON STRETCHED RUBBER VULCANIZATES. I. THE RATE OF CUT GROWTH *

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(WITH AN APPENDIX BY E. D. FARLIE)

INTRODUCTION

The growth of cracks in the surface of stretched components of vulcanized rubber on exposure to the atmosphere is a serious deficiency. It detracts from the appearance, serviceability, and strength, and may lead to early failure. A comprehensive review of the process and the evidence for attributing it to the action of ozone in the atmosphere has been given by Newton[1], the following features being established.

(*1*) The action of ozone on unstretched rubber is slight, no cracks being formed.

(*2*) At small extensions of the order of 10%, cracks appear and grow to form large incisions in the exposed surface.

(*3*) At higher extensions, the number of cracks is larger, but their final size is smaller due to mutual interference. The deterioration of the rubber may be considered less serious, therefore, since the component possesses a finely etched surface rather than one containing a few large cuts.

The basic process appears to consist of the initiation and propagation of a single incision in a deformed rubber under the action of an atmosphere containing ozone. However, the experimental studies that have been reported previously have been concerned with the gross deterioration of an exposed surface when many cracks form simultaneously. It is difficult to deduce from such observations the behavior of a growing incision for the following reasons.

Firstly, the presence of a crack will alter the surface deformations in its neighborhood, and hence may seriously affect the growth of nearby cracks[2]. Secondly, cracks formed on the surface grow simultaneously in length and in depth, the deformation in the region of the growing edges presumably varying with the crack shape as well as with its size. Thirdly, the cracks may propagate by ozone attack at the growing tips and also by attack at points on the surface in close proximity to them. Finally, it is likely that surface irregularities will affect the local deformation, while foreign materials such as dust, decomposition products, or "bloomed" ingredients of the rubber compound may affect the access of ozone.

Although these effects may be of importance in determining the gross deterioration of the surface, it seems reasonable to consider them separately from the basic process. An attempt has therefore been made to examine the latter. In the present part, an experimental study is described of the factors that determine the rate of propagation of a single incision in a thin sheet of

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rubber. In a subsequent part[3] an examination of the conditions which determine whether a crack will form or, being present, will grow is reported.

EXPERIMENTAL METHOD

Conditions of exposure.—The experimental arrangement for producing a steady flow of ozonized oxygen through the test chamber was constructed by E. D. Farlie of these laboratories. It is described in the Appendix, together with the method used for estimating the ozone concentration employed, which ranged from 0.2 to 2.5 mg/l. The rate of flow of gas through the test chamber was held constant at about 25 l/hr. The volume of the test chamber was about 1 l. The gas pressure in the apparatus was only about 1 cm head of water in excess of atmospheric pressure.

TABLE I

MIX FORMULATIONS AND VULCANIZATION CONDITIONS [a]

	Composition, parts by weight				
	Mix A	Mix B	Mix C	Mix D	Mix E
Natural rubber (smoked sheet)	100	—	—	—	—
Butadiene-styrene copolymer (75/25) (Polysar S)	—	100	—	—	—
Butadiene-acrylonitrile copolymer (60/40) (Polysar Krynac 801)	—	—	100	—	—
Butyl rubber (Polysar Butyl 400)	—	—	—	100	—
Polychloroprene (Neoprene GN)	—	—	—	—	100
Zinc oxide	5	5	3	5	5
Stearic acid	1	1	0.5	1	2
Sulfur	2.5	2	1.5	—	—
N-Cyclohexylbenzthiazolesulfenamide	0.6	0.8	—	—	—
Dibenzthiazyl disulfide	—	—	1.0	—	—
Tetramethyl thiuram disulfide	—	—	—	4	—
Light calcined magnesia	—	—	—	—	5
Phenyl-2-naphthylamine	1	1	—	—	1
Vulcanization time at 140° C, min.	40	40	50	50	50

[a] Mix formulations A′ to E′ were as A to E, respectively, but contained, in addition, 25 parts of diethylhexyl adipate and 50 parts of whiting.

In order to carry out measurements at temperatures other than ambient, the test chamber was placed either in a heated water bath or in a bath containing a mixture of ice and water. The incoming gas stream was warmed or cooled before entering the test chamber by passing through a long glass tube immersed in the bath.

Measurement of rate of growth of an incision.—The test pieces consisted of rubber strips 1.5 cm wide and 7 cm long. They were cut from vulcanized rubber sheets, from which the mix formulations and vulcanization conditions are given in Table I.

The test pieces were secured by two light aluminum clamps so that the free length between the clamps was 5 cm. The upper clamp was suspended from a hook in the test chamber roof, and weights were added to the lower clamp to place the central region of the test piece in a state of simple extension. In order to produce a single incision at a convenient position, a small razor cut was made in the center of one edge of the test piece, the surfaces and edges elsewhere being liberally coated with a silicone stopcock grease to prevent ozone attack. A low-power microscope was used to observe the tip of the razor cut and its

growth across the test piece under the action of an atmosphere containing ozone.

It was found that, unless a characteristic well-defined value of the tensile load was exceeded, no growth took place. This feature is discussed in a subsequent part[3]. When the applied tensile stress was adequately large, however, the cut grew linearly across the test piece, finally severing it into two equal pieces. For the major part of its course, the cut grew at a fairly uniform rate, as is shown in Figure 1 (curve I), where the measured cut length is plotted against time for a natural rubber vulcanizate A.

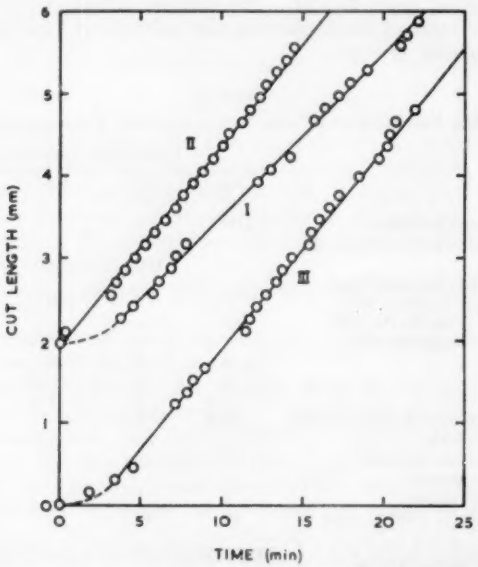

FIG. 1.—Cut growth in an atmosphere containing ozone: (I) initial cut 2 mm long, time measured from the entry of ozone into the test chamber containing the stretched test piece; (II) initial cut 2 mm long, time measured from the application of a tensile stress in a steady atmosphere containing ozone; (III) no initial cut, time measured as in (I).

The apparent induction period seen in curve I is attributed to the interval required for the ozone concentration to reach a steady level in the neighborhood of the test piece, after the gas stream is diverted into the test chamber. To verify this, a similar test piece was subjected to the tensile load after the gas stream had been passing for about ten minutes. The resulting progress of the cut is shown in Figure 1 (curve II). It is clear that growth starts immediately at a steady rate.

In order to confirm that the use of a small razor cut to locate the crack did not affect the subsequent growth, a test piece was prepared without a razor cut. A small region in the center of one edge was left ungreased, and, when a considerably larger tensile load than before was imposed, a cut formed at this site and grew across the test piece under the action of the ozonized atmosphere. The cut length is plotted in Figure 1 (curve III), against time from the entry of the gas stream. The rate of growth is seen to be similar to the previous values.

A series of measurements were made of the rates of cut growth when various loads were applied to the test piece containing a small razor cut about 0.2 cm long. As the imposed stress increased the region around the cut tip subject to attack became increasingly large, and the growing cut changed from a sharp incision to the coarse erosion of a relatively wide strip. However, the rate of propagation was found to be substantially constant for a wide range of imposed stresses, extending from that necessary for the initial cut to grow at all, about 70 g/cm^2, up to a value about ten times as large.

When very large values of tensile stress were imposed, of the order of 2000 g/cm^2, the rate of cut growth was appreciably larger and less well-defined, as might be expected when the imposed stress approaches that required to make the razor cut propagate by simple tearing in the absence of ozone.

For all the vulcanized rubbers examined the rate of cut growth was found to be substantially constant over a considerable range of applied stress, above the minimum value necessary for cut growth to occur. It was also found to be largely independent of the test-piece thickness over the range 0.02–0.2 cm, and hence may be considered appropriate to growth through the bulk rubber. A standard test-piece thickness of about 0.08 cm was chosen for the experiments described subsequently.

In a large number of similar determinations of the rate of cut growth, the measured values were found to vary within the range of $\pm 20\%$ of the mean. This was not considered unacceptable, since relatively large differences in the observed rates were being examined. The scatter is attributed partly to variations in the efficacy of the greasing procedure and partly to fluctuations in the concentration of ozone.

It appears, therefore, that the action of ozone on a stretched rubber vulcanizate can be described by a single parameter, the rate of linear growth of an incision. The effect of the conditions of exposure and the chemical composition of the vulcanizate on this quantity are described below.

Test conditions.—The characteristic rates of cut growth were determined at the normal ozone concentration (1.15 mg/l) and at ambient temperature for test pieces of a number of vulcanized rubbers. The test pieces were about 0.08 cm thick and thoroughly greased on their major surfaces in an attempt to obtain rates characteristic of growth through the bulk. The applied stresses were sufficiently small that the measured rates may be considered typical of the rubbers under light stresses, i.e., where the rate is independent of the applied stress.

EFFECT OF TESTPIECE COMPOSITION

Effect of naturally-occurring impurities.—The measured rate for a dicumyl peroxide vulcanizate of natural rubber (0.08 mm/min) was found to be markedly lower than that for a conventional sulfur vulcanizate A (0.22 mm/min) at an equivalent degree of crosslinking. After extraction with hot acetone for 24 hours in an atmosphere of nitrogen, however, the rates were closely similar, 0.31 and 0.29 mm/min, respectively. The rates were also found to be of this order for both materials when extracted rubber was used in the mix formulations. It appears, therefore, that some acetone-soluble impurity is present in smoked sheet rubber and is capable of surviving the vulcanization reactions when a peroxide system is employed to retard cut growth in the vulcanizate. A conventional sulfur vulcanizing system appears to destroy its efficacy to a large extent, since subsequent extraction has a much smaller effect on a sulfur vulcanizate than on a peroxide vulcanizate.

A peroxide vulcanizate prepared from extracted raw rubber (rate of cut growth of 0.33 mm/min) was swollen in a benzene solution of the extract, after which the benzene was pumped off, to leave the raw rubber extract in the vulcanizate. The rate of cut growth was then found to be 0.07 mm/min; this confirms that the extract contained a potent impurity.

In order to ascertain what natural impurities may act as rate-reducing agents, small amounts of various substances which have been identified in the acetone extract of smoked sheet rubber[4] were added on an open mill to samples of extracted rubber. Peroxide vulcanizates were then prepared and the rates of cut growth determined. It was found that oleic acid effectively retarded cut growth in the vulcanizate, linoleic, and stearic acids, although significantly active, being considerably less efficient. When, for example, 1% of oleic acid was added to the extracted rubber prior to vulcanization with a peroxide system, the measured rate of cut growth for the vulcanizate was found to be 0.105 mm/min, which is near the value obtained when unextracted rubber was used.

Oleic acid (1%) was also added to a test piece of a conventional sulfur vulcanizate A by swelling in from a benzene solution. The measured rate (0.09 mm/min) was comparable to that observed for peroxide vulcanizates.

It seems clear, therefore, that certain impurities present in smoked sheet rubber, notably oleic acid, are capable of reducing the rate of cut growth by a factor of about three. In conventional vulcanizates their action is largely suppressed, presumably because they react with the compounding ingredients.

The rate of cut growth for a peroxide vulcanizate of a butadiene-styrene copolymer (75/25 Polysar S) was also found to be much lower than the value for a sulfur vulcanizate B crosslinked to an equivalent degree. The values obtained after acetone extraction of the vulcanizates were closely similar, however. It seems probable that the cause is similar to that deduced for the natural rubber, namely, the presence in the raw polymer of a rate-reducing impurity.

Effect of vulcanization with TMTD.—The rate of cut growth for extracted natural rubber vulcanized with tetramethylthiuram disulfide (TMTD), zinc oxide, and stearic acid was also found to be small, i.e., 0.08 mm/min. After extracting the vulcanizate the measured rate was 0.32 mm/min, which is closely comparable with that found for conventional sulfur vulcanizates of a similar degree of crosslinking.

It is known that zinc dimethyldithiocarbamate is formed during the TMTD vulcanization reaction. A small quantity (about 3%) of this material was therefore added to the extracted vulcanizate by swelling in from a chloroform solution. The rate of cut growth was then found to be reduced to 0.16 mm/min. It appears, therefore, that an acetone-soluble reaction product of TMTD, probably zinc dimethyldithiocarbamate, can be effective in reducing the rate of cut growth.

TMTD vulcanizates have been reported[5] to show greater resistance to ozone than conventional ones in exposure tests. This is probably due to the lower rate of crack propagation reported above.

The mode of action of such dissimilar materials as zinc dimethyldithiocarbamate and oleic acid is obscure. However, the maximum effect obtained, a reduction in rate by a factor of about three, is small in comparison with the large effects considered in later sections.

Effect of crosslinking.—A number of peroxide and accelerated-sulfur vulcanizates of natural rubber and Polysar S, a butadiene-styrene copolymer (75/25), were extracted with acetone and the rates of cut growth measured.

The corresponding degree of crosslinking of each test pieces was characterized by a measurement of stiffness, the tensile stress necessary to extend the test piece by 25% being determined.

In Figure 2 the rate of cut growth is plotted against the stress at 25% elongation for the vulcanizates of natural rubber and the butadiene-styrene copolymer. It is seen that the rates of cut growth for the two polymers are virtually identical at equivalent degrees of crosslinking. Also, a direct relationship between the rate of cut growth and the degree of crosslinking appears to obtain, the rate decreasing by a factor of about six as the degree of crosslinking increases from an impractically low level to a relatively high one. Only a relatively small variation of the rate of cut growth (a factor of two or three) would be expected due to changes in the degree of crosslinking within the conventional range.

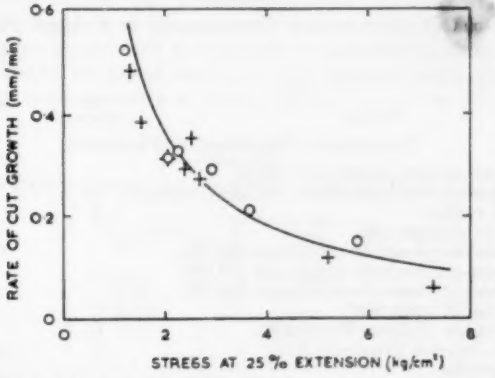

FIG. 2.—Experimental relation between the rate of cut growth and the vulcanizate stiffness (stress at 25% extension) for acetone-extracted vulcanisates of (○) natural rubber and (+) butadiene-styrene copolymer.

The rate of cut growth was found to be inversely proportional to the stress at 25% elongation, i.e., to the number of network chains in unit volume, to a first approximation (Figure 2). It is therefore inversely proportional to the number of chains crossing a randomly positioned plane, as, for example, the plane of propagation of the cut. It seems reasonable that the rate of progress of an ozone cut should vary inversely with the number of chains which have to be severed.

Effect of filler.—Test pieces were prepared from natural rubber mix formulations similar to A but containing, in addition, 45 parts by weight of carbon black (Philblack 0) and 50 parts by weight of whiting, per hundred parts of rubber. It was found necessary to impose markedly higher tensile stresses in order to make a cut grow at all in the ozone atmosphere, and this feature is discussed in a subsequent paper[3]. However, the measured rates of cut growth, 0.30 and 0.28 mm/min, respectively, are similar to the value obtained for the unfilled vulcanizate A (0.23 mm/min), and it appears, therefore, that large quantities of these fillers do not materially affect the characteristic rate of cut growth.

Effect of polymer.—The rates of cut growth were determined on standard test pieces cut from vulcanized sheets of a number of different polymers. The measured rates are listed in Table II.

It appears that the relative resistance to ozone of these rubbers can be associated, at least in part, with the relative rates of cut propagation. Butyl rubber and neoprene, for example, are commonly considered to be ozone-resistant, and the rates are seen to be an order of magnitude lower than for natural rubber and the butadiene-styrene copolymers.

For the butadiene-acrylonitrile copolymers the rate is seen to decrease markedly as the proportion of acrylonitrile increases. It is well known that the molecular mobility decreases also, as is evidenced by a corresponding rise in the rubber-to-glass transition temperature. It seems possible that the observed changes in rate arise from changes in the internal viscosity of the polymer. To examine this, the effect of increasing the molecular mobility by plasticization was studied.

TABLE II

RATES OF CUT GROWTH FOR VULCANIZATES OF VARIOUS POLYMERS

Polymer	Mix reference	Rate of cut growth, mm/min at 1.15 mg ozone/l.
Vulcanizates Containing No Plasticizer		
Butadiene-styrene copolymer (95/5)	—	0.22
Butadiene-styrene copolymer (75/25) (Polysar S)	B	0.37
Natural rubber	A	0.22
Synthetic polyisoprene	—	0.245
Butadiene-acrylonitrile copolymer (82/18)	—	0.22
Butadiene-acrylonitrile copolymer (70/30)	—	0.055
Butadiene-acrylonitrile copolymer (60/40) (Polysar Krynac 801)	C	0.04
Butyl rubber (Polysar Butyl 400)	D	0.02
Polychloroprene (Neoprene GN)	E	ca. 0.01
Gutta-percha	—	0
Chlorosulfonated polyethylene (Hypalon)	—	0
Vulcanizates Containing 25 Parts of Diethylhexyl Adipate		
Butadiene-styrene copolymer (75/25) (Polysar S)	B′	0.40
Natural rubber	A′	0.26
Butadiene-acrylonitrile copolymer (60/40) (Polysar Krynac 801)	C′	0.20
Butyl rubber (Polysar Butyl 400)	D′	0.24
Polychloroprene (Neoprene GN)	E′	0.05

Effect of plasticization.—Vulcanized test pieces were prepared similar to those described above but containing, in addition, 25 parts by weight of an ester plasticizer, diethylhexyl adipate, per hundred parts of polymer. Also, 50 parts by weight of an inert filler, whiting, were added to assist the incorporation of the plasticizer; it has been noted earlier that this ingredient appears to have virtually no effect on the cut growth rate.

The measured rates of cut growth for the plasticized materials are given in Table II for comparison with the original values. Natural rubber and the 75/25 butadiene-styrene copolymer which were originally subject to rapid cut growth are seen to be little affected by plasticization. However, the relatively viscous polymers, butyl rubber and the 60/40 butadiene-acrylonitrile copolymer, exhibited cut growth rates many times larger than before, and similar to that for the first two materials. It appears, therefore, that the low rates ob-

served for the unplasticized materials are primarily due to their high internal viscosity.

The plasticized polychloroprene is seen to show more rapid cut growth than the unplasticized sample, but the value is still very low.

EFFECT OF TEST TEMPERATURE AND OZONE CONCENTRATION

Effect of temperature of test.—Measurements were made of the characteristic rates of crack growth for a number of the vulcanized rubbers described in the previous section, at several temperatures in the range 0–80° C. The ozone concentration employed was 1.15 mg/l.

The results obtained for four of the materials at temperatures of 2, 20, and 50° C are given in Table III. Erratic cut growth was found at 80° C for all the materials except the natural rubber vulcanizate, probably due to incipient tearing. The results obtained were generally similar to those at 50° C. Similar difficulties were experienced with the plasticized materials at elevated temperatures, probably due to the same cause, but the measurements again indicated that substantially the same rates of cut growth obtained over the temperature range 20–80° C.

TABLE III

RATES OF CUT GROWTH FOR FOUR POLYMERS AT 2, 20, AND 50° C

Mix reference	Cut growth, mm/min		
	2° C	20° C	50° C
A	0.15	0.22	0.19
B	0.13	0.37	0.34
C	0.004	0.04	0.23
D	—	0.02	0.16

It is seen in Table III that the rates of cut growth for the relatively viscous materials C and D are strongly dependent on temperature. This is in accord with the conclusion of the previous section, that the internal viscosity determines the rate of cut growth for these materials.

It also appears that, provided a minimum degree of segmental mobility is present, further increases in mobility do not act to increase the rate of cut growth. Natural rubber A and the 75/25 butadiene-styrene copolymer B appear to possess adequate molecular mobility, even at 2° C, although the cut growth is somewhat retarded at this temperature, particularly for the latter material. In consequence, raising the test temperature and incorporating plasticizer have only minor effects on the rate of cut growth. In butyl rubber D and the 60/40 butadiene-acrylonitrile copolymer C, on the other hand, the motion of molecular segments appears to be so slow under normal conditions that it restricts the rate at which a cut can advance. Hence it is only at elevated temperatures or when plasticizer is incorporated, that the molecular mobility becomes sufficiently great to cause no impedance to the progress of the cut. Thereafter, further increases in molecular mobility have no effect.

It might be concluded that the four polymers have similar reactivities to ozone, since the maximum rates attained are not dissimilar, namely 0.2–0.4 mm/min. It seems probable, however, that the reactivities are sufficiently high for the maximum rates to be governed largely by the rate of incidence of ozone, the reaction of each incident molecule being completed before the arrival of the next.

The rates of cut growth for the neoprene test pieces were found to be somewhat increased by raising the temperature, although at 80° C the rate was still relatively low (of the order of 0.05 mm/min). The markedly lower rates, which are retained at elevated temperatures and after plasticization, indicate that the intrinsic reactivity of this material is considerably smaller, as its chemical composition might suggest.

It is interesting to note that no growth could be induced in crosslinked gutta-percha at room temperature when the material is highly crystalline. At 80° C, however, when it is amorphous and rubberlike, cut growth took place at a rate comparable to that for the natural rubber vulcanizates. This behavior also suggests that no cut growth can occur if the polymer chains are immobile.

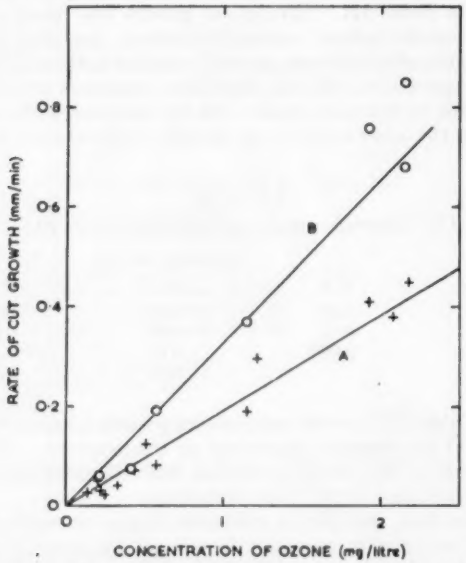

FIG. 3.—Experimental relations between the rate of cut growth and the concentration of ozone for vulcanizates of (+) natural rubber A and (○) butadiene-styrene copolymer B.

Effect of ozone concentration.—The characteristic rates of cut growth were determined over a range of ozone concentrations at ambient temperature. The concentrations employed ranged from about 0.1 to 2.5 mg of ozone/l.

In Figure 3 the rate of cut growth is plotted against the ozone concentration for natural rubber A and the 75/25 butadiene-styrene copolymer B, representative of relatively rapidly-attacked materials. Substantially linear relations are seen to obtain within the limited experimental accuracy, the rate of cut growth being directly proportional to the concentration of ozone. A similar dependence was found to obtain for the plasticized polymers. The rates for the more slowly attacked polymers were found to increase with increasing concentration also, but the measurements were, in general, insufficiently accurate to establish the form of dependence. The measurements for the 60/40 butadiene-acrylonitrile copolymer C are plotted in Figure 4, and are seen to suggest a departure from linearity at high concentrations, the rates being lower than a linear relation would predict.

The direct proportionality found for the vulcanized natural rubber A, for example, may be used to obtain a rough estimate of the effects of exposure to a normal outdoor atmosphere, where the concentration of ozone is about 7×10^{-5} mg/l[1]. The corresponding rate of cut growth is predicted to be about 1.3×10^{-5} mm/min, by means of the linear relation shown in Figure 3. Hence, the first signs of deterioration, which might be taken as the presence of surface cracks 0.2 mm long, would be noticed after 7.5×10^3 min (about 5 days). This figure is in good agreement with observations of the time necessary for visible deterioration to occur in outdoor exposure tests.

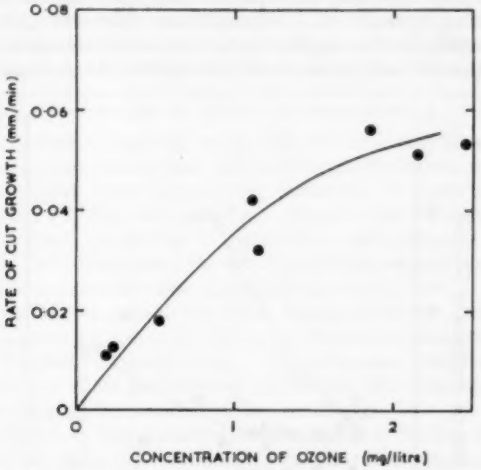

FIG. 4.—Experimental relation between the rate of cut growth and the concentration of ozone for a butadiene-acrylonitrile copolymer C.

It has been noted in the preceding section that the rates of cut growth in natural rubber, the butadiene polymers, and butyl rubber are similar when the restricting effect of hindered molecular motion is overcome by plasticization or raising the temperature. It now appears that the rate depends directly on the concentration of ozone, so that for the four polymers the rate is given approximately by (0.2 mm/min)/mg of ozone/l.

CUT GROWTH IN THIN TEST PIECES

The study of cut growth in various materials and under various exposure conditions was carried out with specimens greased on their major surfaces to restrict the attack of ozone to the tip of the growing cut. A subsidiary series of measurements was made using test pieces of the natural rubber vulcanizate A, with a narrow central strip across the test piece (the region through which the cut advanced) left *ungreased*, since this is more representative of conventional test methods.

It was found in preliminary experiments that cracks tended to form ahead of the growing incision, particularly in the thinner test pieces, yielding high, irregular rates of growth. This difficulty was overcome by the use of test pieces cut from sheets molded between clean glass plates and having smoother major surfaces. The experimental irreproducibility was, unfortunately, still

large, as is evident in Figure 5, where the experimental results are portrayed. However, major differences are shown in Figure 5, the thinner test pieces exhibiting more rapid cut growth at any given value of the imposed tensile stress and a greater dependence of the rate of growth on the imposed stress. The increased rate in the thin test pieces is ascribed to the following mechanism.

It is assumed that, for a short distance d ahead of the growing cut, the local tensile stress exceeds that necessary for ozone attack to occur, and a cut may therefore be propagated by attack from the major surfaces immediately ahead of the tip. For sufficiently thin test pieces, i.e., when d is much greater than the thickness, this process may take place rapidly in comparison with the normal growth, leading to rapid crack propagation. Moreover, since the distance d will clearly increase as the applied tensile stress is increased, the rate of cut growth for the thinner test pieces would be expected to increase similarly, as is

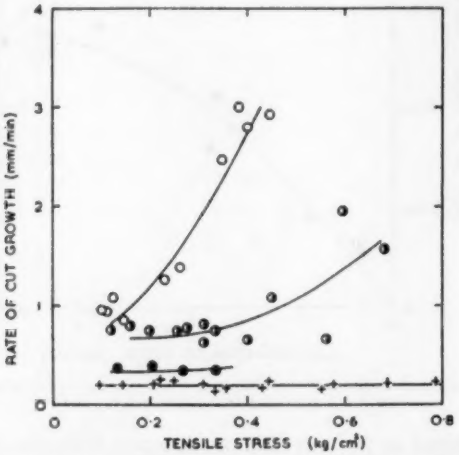

FIG. 5.—Experimental relations between the rate of cut growth and applied tensile stress for various test-piece thicknesses: (○) 0.25 mm; (◑) 0.65 mm; (●) 2.0 mm: (+) 0.6–2.0 mm (greased on major surfaces).

observed experimentally. It has been found possible to predict approximately the relative rates of cut growth by such a treatment, but the experimental scatter renders the agreement obtained of doubtful significance. However, the mechanism proposed, namely attack in advance of the crack tip, provides a satisfactory qualitative explanation of the observations.

When the surfaces between which the cut grew were protected from ozone attack by a thick coating of silicone grease, the observed rates of growth were small and largely independent of the test-piece thickness or the applied tensile stress over the range employed (100–1000 g/cm^2). There was still some tendency for the thinner test pieces to show more rapid growth, presumably due to failure or disturbance of the grease film caused by the propagation of the crack. A standard test-piece thickness of about 0.08 cm was chosen for the experiments described in the previous sections, and all test pieces had their major surfaces covered with grease. The measured rates of cut growth should therefore be appropriate to growth through the bulk, to a first approximation.

It has frequently been reported that cracks form (i.e., grow to a visible size) more rapidly in the surface of highly stretched rubber[1,2]. The present observa-

tions suggest that this is due to attack in advance of the growing crack tip. The rate of growth of a surface crack may therefore not be representative of the rate of attack.

GENERAL CONCLUSIONS

(*1*) It has been found that a cut in the edge of a stretched sheet of rubber grows across it at a constant rate in an atmosphere containing ozone. In thin sheets the rate is increased, apparently by attack of ozone in advance of the growing cut. This effect may be greatly reduced by coating the major surfaces of the test piece with silicone grease, when the measured rate is assumed to be characteristic of growth through the bulk.

(*2*) Provided the applied tensile stress exceeds a well-defined critical value, the cut advances at a rate substantially independent of the applied stress until the stress approaches the much larger value sufficient to cause tearing in the absence of ozone.

(*3*) The characteristic rates of cut growth for natural rubber (smoked sheet) and a butadiene-styrene copolymer (75/25 Polysar S) depend on the vulcanization system employed, being appreciably lower for peroxide and tetramethylthiuram disulfide (TMTD) vulcanizates. In peroxide vulcanizates, the effect is attributed to small quantities of impurities, notably oleic acid in natural rubber. In TMTD vulcanizates the effect is attributed to a product of the vulcanization reaction, probably zinc dimethyldithiocarbamate.

(*4*) The rates of cut growth for clean vulcanizates, i.e., acetone-extracted ones, are very similar for natural rubber and the butadiene-styrene copolymer at equivalent degrees of crosslinking. The rates are decreased by increased crosslinking, but the effect is relatively small over the conventional range, the measured rates varying by a factor of two or three.

(*5*) The inclusion of large quantities of whiting or carbon black in the mix formulation appears to have little effect on the characteristic rate of cut growth.

(*6*) The more viscous polymers, a butadiene-acrylonitrile copolymer C and butyl rubber D, exhibit slower cut growth than the relatively mobile ones, A and B, at room temperature. On raising the temperature or on plasticization, however, the observed rates were increased markedly to approach those observed by materials (A and B) which are virtually unaffected by these changes. It is concluded therefore, that the rate of cut growth is limited in relatively viscous polymers by the restricted mobility of polymer chains.

(*7*) Specific effects are suggested in the case of polychloroprene E, which exhibited much slower cut growth under all conditions, and chlorosulfonated polyethylene, which appeared to be completely resistant to ozone.

(*8*) The similar rates of cut growth observed for the relatively mobile polymers A and B and the plasticized plymers A′ — D′ were found to be directly proportional to the concentration of ozone to a first approximation, the rates being of the order of (0.2 mm/min)/mg of ozone/l.

APPENDIX: LABORATORY PREPARATION OF OZONIZED OXYGEN

E. D. Farlie

Ozone was produced by the ultraviolet irradiation of oxygen[6], which was passed through a glass vessel enclosing a quartz low-pressure mercury discharge lamp (Mercury Vapour Burner, Type T/M5/369, the Thermal Syndicate, Ltd.,

London). A reducing valve, a constant-head leak, and a flowmeter were incorporated before the generator to control and measure the rate of flow of oxygen. A cooling coil immersed in an ice-water mixture was also included at the inlet to the ozone generator, as this provision was found to reduce fluctuations in the ozone concentration.

The output concentration of ozone was found to be largely independent of the rate of flow of oxygen over the range 2–25 l/hr. To provide lower concentrations at a constant rate of flow of 25 l/hr, a separately controlled stream of oxygen was used to dilute the output from the generator.

The combined gas stream was led either through the test chamber to an estimation column or to a destroyer vessel containing soda lime, which was found, in contrast to other experience[7], to remove ozone efficiently from a gas stream passing through it.

For estimation, the gas stream was passed up a vertical glass column, 2.5 cm in diameter and 45 cm long, packed with broken glass tubing[8]. A neutral 5% solution of potassium iodide[9] was allowed to pass down the column at a rate of about 1 drop/sec to a collecting flask at the bottom. After a period of time, generally about 20 min, the gas stream was diverted to a destroyer vessel. The column was then rinsed with distilled water, and the contents of the collecting flask were acidified with 2*N* sulfuric acid[9] and titrated immediately with a standard solution of sodium thiosulfate.

The following additional precautions were observed. (1) The potassium iodide solution was stored in the dark and shielded from direct light while in use. (2) The sodium thiosulfate solution was also stored in the dark, and was frequently standardized against a standard solution of potassium dichromate. It contained 1 ml/l of chloroform to inhibit bacterial action[10]. (3) Before admitting the gas stream, the estimation column was rinsed out with the potassium iodide solution.

The concentration of ozone was calculated from the measured titer and the flow rate, by using the relation 1 ml of 0.1*N* sodium thiosulfate = 2.4 mg of ozone.

SYNOPSIS

Experimental measurements are described of the propagation of a cut through a stretched rubber sheet under the action of an atmosphere containing ozone. It is shown that a well-defflned rate of cut growth may be determined which is characteristic of growth through the bulk and substantially independent of the applied tensile stress when this exceeds a critical value necessary for growth to occur at all. The effect of the polymer employed, the vulcanization system used, the degree of crosslinking, and the presence of fillers andplasticizers on the characteristic rate of cut growth is examined. The effects of temperature in the range 2–80° C and ozone concentration in the range 0.2–2.5 mg. of ozone/l are also studied. It is concluded that the rate at which a cut advances in highly reactive polymers is principally determined by the rate of incidence of ozone molecues and, for rrelatively viscous polymers, by the restricted mobility of polymer chains. The degree of crosslinking and the vulcanization system adopted appear to be a secondary importance, while the presence of fillers has a negligible effect.

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THE ATTACK OF OZONE ON STRETCHED RUBBER VULCANIZATES. II. CONDITIONS FOR CUT GROWTH *

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INTRODUCTION

In Part I[1] an experimental study was reported of the factors determining the rate of propagation of a cut through a stretched rubber sheet under the action of an atmosphere containing ozone. It was remarked that no growth took place from a small razor cut made in one edge of the test pieces unless a critical value of the applied tensile stress was exceeded. The value was quite small, of the order of 100 g/cm^2 for a soft natural rubber vulcanizate.

In the present part an examination is reported of the conditions necessary for a crack to form or, being present, to grow.

EXPERIMENTAL METHOD

The experimental arrangement for producing a steady flow of ozonized oxygen through the test chamber has been described previously[1]. The concentration used in the present work was generally 1.15 mg of ozone/l. The test pieces consisted of rubber strips 1.5 cm wide and 7 cm long, of various thicknesses in the range 0.02 to 0.2 cm. They were cut from vulcanized rubber sheets for which the mix formulations and vulcanization conditions were given in Table I of Part I[1].

Each test-piece was suspended by a clamp from the roof of the test chamber, and weights were added to a light lower clamp placing the central region of the test piece in simple extension. The whole of the test piece, except for the region under observation, was coated with a silicone stopcock grease to prevent ozone attack. The applied weight was varied to determine the minimum value at which cracks appeared in the exposed region or at which a cut initially present grew a detectable amount during a fixed period of exposure. The period was chosen so that growth at a rate one-twentieth of that obtaining under moderately large stresses could be detected. For the natural rubber vulcanizate A, for example, which exhibited a rate of cut propagation of about 0.2 mm/min at adequately large applied stresses, the observations were continued for 15 min. With the low power microscope employed, growth of a cut by 0.1 mm could be detected.

It was found, however, that an intermediate rate of cut growth was never observed. Either the cut did not grow by a visible amount, even in exposure times of more than one hour, or the rate of growth was the constant value found for a wide range of stresses above the critical level.

The threshold stress necessary for cut growth to occur might arise from some physical barrier initially present at the cut tip, due to oxidative degradation

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of the surface layer, for example. The observed critical stress would then be that necessary to disrupt the protecting layer and allow the attack of ozone on the underlying rubber. In order to examine this possibility a test piece with a small razor cut in the center of one edge was prepared and placed in the test chamber with a tensile stress applied of 0.096 kg/cm², somewhat greater than the critical value. After the cut had grown by about 2 mm the applied stress was reduced abruptly to 0.046 kg/cm² (below the ctirical amount). The cut was found to stop immediately. It appears therefore that the critical stress does not arise merely from the presence of a protecting film initially present at the cut tip.

TABLE I

EFFECT OF SIZE OF EXPOSED AREA

Diameter of exposed area, mm	Observed cracking stress, kg/cm²
7.75	0.8
3.65	0.8
2.70	1.2
1.35	2.4
0.68	>2.6

EFFECT OF TEST CONDITIONS

Effect of length of razor cut on critical stress.—The critical applied tensile stress was determined for test pieces of a soft natural rubber vulcanizate A. It was found to be largely independent of the test-piece thickness, but to depend markedly on the length of the razor cut, as shown in Figure 1, where the measured values are plotted against the initial cut length.

The tensile stress S_t at the tip of a sharp cut may be calculated by means of classical elasticity theory[2] in terms of the applied tensile stress S, the cut length l, and its effective radius r at the tip:

$$S_t = S[1 + 2(l/r)^{\frac{1}{2}}] \tag{1}$$

If it is assumed that a cut will propagate under the action of ozone when the tensile stress at the tip exceeds a characteristic value S_t, the relation between the stress in the bulk S necessary for cut propagation and the cut length l should be given by eq. (1). When l is many times the tip radius r, as seems probable for the razor cuts considered, eq. (1) becomes

$$S = S_t r^{\frac{1}{2}}/2l^{\frac{1}{2}} \tag{2}$$

The solid curve in Figure 1 is of this form, and is seen to describe the results with fair success in view of the limited experimental accuracy and the approximations in the theory. The quantity $S_t r^{\frac{1}{2}}$ was chosen to give agreement with the experimental results, the value obtained in this way being 0.10 kg/cm$^{\frac{1}{2}}$. Microscopic examination suggested that r had a value of 10^{-3} cm or even smaller, corresponding to a value for S_t of 3.2 kg/cm² or greater.

From the measured stress-strain relation in simple extension for the vulcanizate employed, the corresponding critical extension at the tip of the cut is 28% or more. This is probably too large for the classical treatment based on infinitesimal strains to apply accurately, and hence the predictions of Equation (2) might be expected to be quantitatively in error, the calculated values of S_t

and the critical extension at the tip being particularly uncertain. However, the theoretical predictions are seen to be qualitatively in accord with experiment, and it therefore appears that the basic assumption—that a characteristic critical tensile stress is necessary at the crack tip for growth to occur—is correct. The value required appears to be relatively large, as the measurements reported below confirm.

Effect of surface finish.—Measurements were made of the applied tensile stress necessary to cause a crack to appear in a small region at one edge of the test piece which was greased to prevent ozone attack at sites other than the one under observation. When the test piece was prepared by cutting with scissors from a vulcanized rubber sheet, the critical stress was irreproducible, varying between 0.45 and 0.90 kg/cm^2. When the test piece was molded so that the exposed edge had been formed against a machined metal surface, a more reproducible value of about 0.85 kg/cm^2 was obtained.

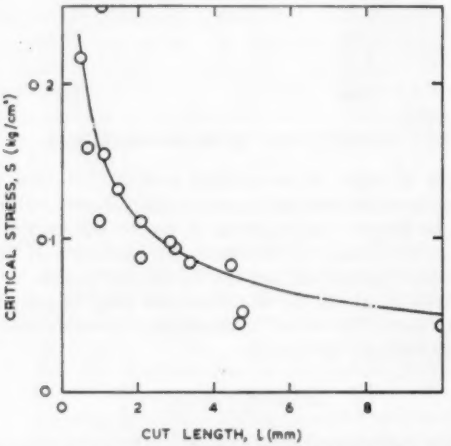

FIG. 1.—Relation between the minimum applied stress S for cut growth and the cut length l. The full curve is of the form given in eq. (2).

Although these values are considerably higher than the critical stresses observed for test pieces containing razor cuts (Fig. 1), it is probable that irregularities still exist in the exposed surfaces so that the values observed are not measures of the local critical tensile stress S_t. In an attempt to improve the surface smoothness, fresh test pieces were prepared by cutting from sheets molded between clean glass plates. A small circular area was left ungreased in the center of one major surface instead of at one edge as in the previous measurements, and the critical values of the applied stress determined. They were found to average 1.50 kg/cm^2.

Even the glass-molded surfaces are likely to contain some flaws, as discussed below. It appears therefore that the critical stress S_t for cut propagation is greater than 1.5 kg/cm^2. This conclusion is in general accord with that deduced from the measurements on test pieces containing razor cuts.

Effect of size of exposed area.—Using test pieces cut from a peroxide-vulcanized natural rubber sheet molded between clean glass plates, measurements were made of the applied tensile stress necessary for cracks to appear in a small,

roughly circular region left ungreased in the center of one major surface. The values obtained for the critical applied stress are given in Table I for various diameters of the exposed area.

They are seen to increase as the size of the exposed area is reduced, until at the smallest diameter the protecting grease film failed, and cracks formed elsewhere in the test piece. It seems probable that there is a distribution of surface irregularities, deep flaws being sparsely distributed and hence not likely to occur within small exposed areas.

Depth of surface flaws.—It is possible to calculate by means of Equation (2) the depth of a razor cut which would require a critical stress for propagation of the order of that observed for test pieces with molded surfaces, i.e., 1–2 kg/cm^2. The value obtained is 0.5×10^{-3} to 2×10^{-3} cm.

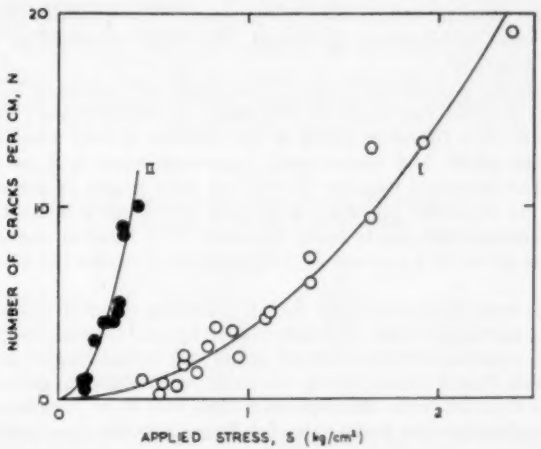

FIG. 2.—Relations between the number N of cracks formed per unit length of an exposed edge and the applied tensile stress S: (I) when the edge is formed by die-cutting; (II) when the edge contains numerous small razor cuts. The full curves are of the form given in eq. (4).

It does not seem improbable that flaws of this order of magnitude exist in molded surfaces. They might arise, for example, from the presence of particles of foreign matter in the rubber, apart from imperfections in the mold surface.

Number of cracks formed.—Test pieces having one vertical edge left ungreased were exposed in the test chamber with varying applied stresses. Cracks formed at several points on the edge and grew across the test piece a at uniform rate. In Figure 2 the number of cracks formed per unit length of the exposed edge are plotted against the applied tnesile stress for test pieces stamped out with a die from sheets of the soft natural rubber vulcanizate A. The experimental results are represented by open circles.

If it is assumed that many flaws exist in the die-cut edge, each of length l and tip radius r, the stress at the tip of each is given by classical elasticity theory[3] in the form

$$S_t = S[1 + 2(d/\pi r \tan \mathrm{h}\, \pi l/d)^{\frac{1}{2}}] \qquad (3)$$

where S is the applied tensile stress and d is the distance between adjacent flaws. Crack growth will occur when the stress at the tip of each crack exceeds

the critical value S_t. The maximum value of the quantity $\tanh \pi l/d$ is unity, and hence the minimum possible crack separation d is

$$d = (\pi r/4)(S_t - S)^2/S^2$$

As the applied stress S is considerably smaller than the value S_t necessary at the crack top to cause propagation, this relation may be simplified to yield

$$N = 1/d = 4S^2/\pi S_t^2 r \tag{4}$$

where N is the maximum possible number of cracks which may occur per unit length.

Curve I of Figure 2 is of the form given in Equation (4) and is seen to describe the experimental results with fair success. The quantity $S_t^2 r$ was chosen to give the most satisfactory agreement; the value obtained in this way for $S_t r^{\frac{1}{2}}$ was 0.59 kg/cm$^{\frac{1}{2}}$.

The parameter governing the density of cracks $S_t r^{\frac{1}{2}}$ is similar to that governing the effect of initial cut length on the observed critical stress [Equation (2)]. Measurements were therefore made of the number of cuts which grew from a test-piece edge which had many small razor cuts made in it, at about 1 mm spacings. The observed number of cuts per unit length of the exposed edge which grew on exposure to ozone is plotted in Figure 2 against the applied stress, the experimental points being represented by filled-in circles. Curve II is of the form given in Equation (4); it is seen to describe the results satisfactorily.

The value used for the quantity $S_t r^{\frac{1}{2}}$ in obtaining curve II was 0.135 kg/cm$^{\frac{1}{2}}$, in reasonable agreement with the value of 0.10 kg/cm$^{\frac{1}{2}}$ obtained previously from the observed relation between critical stress and initial length of a razor cut. The hypothesis that a critical stress condition at the flaw tip governs the onset of crack growth in an ozone atmosphere is thus seen to be capable of predicting the bulk stress required to make cuts of different lengths grow, and the number of cuts which grow out of many initial ones, in terms of a single parameter. In a later section this parameter is considered from a different viewpoint, as a measure of the energy necessary for crack growth.

It has frequently been observed that the number of cracks formed per unit area of an exposed surface increases as the applied stress is increased. Such measurements are, however, not readily compared with those reported above, of the number of cracks formed per unit length, although they are qualitatively in agreement.

EXPERIMENTAL RESULTS

Test conditions.—In order to compare the values of critical stress for various rubbers, test pieces were prepared with a razor cut about 2 mm long in the center of one vertical edge and the applied stress necessary for growth determined. It is possible that the effective radius of the tip of a razor cut is somewhat different for rubbers of very different properties, and measurements were therefore also made of the applied stress necessary to cause cracks to appear in a small, ungreased, circular region, about 3 mm in diameter, in the center of a glass-molded surface. The two methods of measurement are denoted by method 1 and method 2, respectively.

To obtain relatively uniform razor cuts for the Method 1 measurements, a procedure similar to that described by Buist and Kennedy[4] was adopted. The

test piece was secured between flat metal plates and the edge of the razor blade passed through a narrow slot in them.

The critical stress was found to be greater for a test piece exposed repeatedly under gradually increasing load than for one without previous exposure. It seems likely that ozone attack occurs at tensile stresses below the critical amount, but is restricted to the surface regions. Such attack would render the tips of the initial cuts or flaws less sharp and hence necessitate a higher stress for growth.

In the measurements described below, a new test piece was exposed at each load, the values being decreased until crack growth did not occur. The critical stress values obtained for vulcanizate A were, therefore, only about one half of those determined previously.

Effect of vulcanizate stiffness.—Values were obtained by Method 2 of the critical applied stress S_2 for dicumyl peroxide (DCP) vulcanizates of natural rubber and a conventional sulfur vulcanizate A. The results are given in Table II together with the values of Young's modulus E for each vulcanizate determined by measurements of the load-extension relations for small extensions, and the extension e_2 corresponding to the observed critical stress S_2.

TABLE II

CRITICAL CONDITIONS FOR CRACK FORMATION IN NATURAL RUBBER VULCANIZATES

Vulcanizate	Young's modulus E, kg/cm²	S_2, kg/cm²	e_2, %	$W \times 10^{-6}$, ergs/cm³
1½% DCP	4.5	0.80	21.0	8.3
3% DCP	9.6	1.35	15.0	10.5
6% DCP	14.3	1.45	10.5	8.1
Sulfur vulcanizate A	15.0	1.50	10.4	8.1

The experimental measurements of critical stress were somewhat inaccurate. Moreover, the different vulcanization systems employed may well affect the type and number of surface flaws and hence the applied stress necessary to produce a critical condition at the flaw tips. Within these limitations, however, it appears that neither the critical stress nor the extension is independent of vulcanizate stiffness. To a first approximation, the stored elastic energy W appeared to be constant, the values obtained from the areas under the stress-extension curves up to the critical point being given in the last column of Table II. This observation is discussed in a later section.

The critical stress was also determined for a vulcanizate similar to A, but containing in addition 45 parts by weight of carbon black (Philblack O) per hundred parts of rubber. The value obtained was 3.8 kg/cm², considerably larger than that for the soft, unfilled vulcanizates. If, however, a similar value of the stored elastic energy is required, a substantially higher value of critical stress would be exptected for such a stiff rubber. It was found from the experimentally-determined stress-extension relation that a value of the stored elastic energy similar to those listed in Table II obtained at an applied stress of 3.0 kg/cm², in fair agreement with the observed critical stress. To a first approximation, therefore, it appears that the higher critical stress observed for the filled vulcanizate is merely a reflection of its enhanced stiffness.

Effect of vulcanization system employed.—Measurements were made of the critical stress for dicumyl peroxide (DCP), tetramethylthiuram disulfide

(TMTD), and conventional sulfur vulcanizates. No significant difference was found between the critical stress values determined by Method 2 for the peroxide and the conventional vulcanizate A (1.50 and 1.45 kg/cm²) respectively. A markedly lower value (0.38 kg/cm²) was obtained for the TMTD vulcanizate, however. It was noted that the glass-molded surface for this test piece was not as smooth in appearance, due to the presence of a "bloomed" material, and the low critical stress is considered to arise from the presence of flaws associated with this inferior surface finish. The value of critical stress determined by Method 1 when a razor cut is made in the test piece was found to be similar to that for the DCP vulcanizate and somewhat larger than that for the conventional sulfur vulcanizate A.

In Part I the presence of extractable materials in DCP and TMTD vulcanizates was shown to reduce the rate of cut growth considerably. The measurements reported above suggest that the effect of these materials on the critical stress required for crack growth is relatively slight.

Effect of polymer.—The critical stress values were determined by the two experimental methods for vulcanizates of a number of polymers. The results are given in Table III.

TABLE III

CRITICAL STRESS VALUES FOR VULCANIZATES OF VARIOUS POLYMERS AT 20 AND 50° C

Polymer	Mix reference	E, kg/cm²	S_1, kg/cm²		S_2, kg/cm²		S_2', kg/cm²
			20° C	50° C	20° C	50° C	
Natural rubber	A	15.0	0.065	0.055	1.23	1.18	1.50
Butadiene-styrene copolymer (75/25) (Polysar S)	B	12.5	0.064	0.045	1.06	—	1.35
Butadiene-acrylonitrile copolymer (60/40) (Polysar Krynac 801)	C	13.2	0.070	0.068	0.97	1.13	1.40
Butyl rubber (Polysar Butyl 400)	D	7.4	0.12	0.23	0.91	0.68	1.02
Polychloroprene (Neoprene GN)	E	25.0	0.21	—	2.30	—	2.00

The values obtained by Method 1 for the butyl rubber vulcanizate D are seen to be considerably larger than those for A, B, and C. However, the initial razor cuts appeared to be of a somewhat different character in this material and they may well have been less sharp. The results by Method 2 are comparable for the four materials.

The polychloroprene vulcanizate E exhibited a considerably higher critical stress in both experimental arrangements. It was, however, appreciably stiffer than the other materials. The values of Young's modulus E determined from the measured stress-extension relations at small extensions are given in Table III and also the values of the applied stress S_2' at which the stored elastic energy was found to be 8.2×10^4 ergs/cm³, the critical value obtained previously for a series of natural rubber vulcanizates. The values obtained for S_2' are seen to be in reasonable accord with the experimental values of the critical stress S_2.

It is concluded, therefore, that, to a first approximation, the critical condition is similar for all the polymers, i.e., that the stored elastic energy in the bulk rubber should have a characteristic value of about 10^5 ergs/cm³ for attack to take place on a glass-molded surface. A razor cut 2 mm in length appears to constitute a "flaw" of differing severity in different polymers. The corresponding values of the critical stored energy range between 10^2 and 10^3 ergs/cm³.

Measurements were also made of the critical stress for vulcanizates containing 25 parts by weight of an ester plasticizer, diethylhexyl adipate, per hundred parts of polymer. The values obtained by both Method 1 and Method 2 were generally similar to those for the unplasticized vulcanizates given in Table III. It appears, therefore, that the critical conditions for ozone attack are largely independent of the segmental mobility of the polymer molecules, in marked contrast to the rates of cut growth[1].

Effect of test temperature and concentration of ozone.—A limited number of measurements were made of the critical stress at a temperature of 50° C for both plasticized and unplasticized vulcanizates, the results for the latter being included in Table III. They were similar to the values obtained at 20° C and suggest that the critical conditions do not depend markedly on temperature.

The critical stress was also determined by Method 2 for the natural rubber vulcanizate A at a concentration of ozone of 0.23 mg/l i.e., about one fifth of that normally employed. The value obtained, 1.13 kg/cm^2, is closely comparable to that found at the normal ozone concentration, namely, 1.23 kg/cm^2, and it appears that the critical condition does not vary markedly with ozone concentration.

CHARACTERISTIC ENERGY FOR CRACK PROPAGATION

The stored elastic energy W in the bulk rubber is related to the energy T available for cut propagation at the tip of a cut of length l by the relationship[5]:

$$T = 2KlW \tag{5}$$

where K is a numerical quantity having a value[5] of about 2. The observation in preceding sections that the stored energy W is substantially constant for a number of natural rubber vulcanizates and for vulcanizates of a numer of polymers thus indicates that a characteristic energy T is required at the flaw tip for growth to occur in an atmosphere of ozone. A similar characteristic energy criterion has been proposed by Griffith[6] to account for the observed strength of glass, and has been shown by Rivlin and Thomas[5] to govern the tearing of rubber.

The Equation (5) may be transformed to yield the dependence of the critical bulk stress S upon the crack length l, in the form

$$S = (TE/Kl)^{\frac{1}{2}} \tag{6}$$

where E is Young's modulus for the rubber, the extensions of the bulk rubber being assumed sufficiently small for a linear stress extension relation to apply. An equivalent relation is given in Equation (2) and has been shown to predict the form of the observed dependence of the critical stress upon the length of an initial razor cut.

The values of the critical stress S for vulcanizates of natural rubber A and of a butadiene-styrene copolymer B were found to be about 65 g/cm^2 for test pieces with an initial razor cut of 2 mm length. The corresponding values of T may be calculated from Equation (6) by use of the measured values of Young's modulus E. The values obtained in this way are about 120 ergs/cm^2. In contrast, the characteristic energies for tearing similar vulcanizates are much higher[7], of the order of 10^6 ergs/cm^2.

Somewhat greater values of critical stress, and hence T, obtain for the other

polymers, where it seems likely that the initial razor cuts are less sharp. Indeed, the present value of about 120 ergs/cm^2 is only realized with carefully controlled incisions, and significantly lower values were never obtained. It appears therefore that the characteristic energy for ozone attack is extremely low in comparison with that for tear propagation, but somewhat larger than would be expected as a measure of twice the surface energy of the newly formed surfaces, when a value of about 50 ergs/cm^2 would be anticipated[8]. The discrepancy might arise from slight adhesion of the newly formed surfaces.

GENERAL CONCLUSIONS

(*1*) It has been found that a cut in the edge of a stretched sheet of rubber will not grow in an atmosphere of ozone unless the applied tensile stress exceeds a well-defined critical value. Moreover, if the stress is subsequently reduced below the critical amount, the cut stops. The critical stress appears therefore to be a property of the rubber rather than of a barrier layer at the surface.

(*2*) The critical stress for ozone attack is found to depend on the cut length in nicked test pieces and on the surface smoothness of unnicked test pieces, in accordance with a proposed criterion for crack growth to occur, that the stress at the tip of the cut or surface flaw should exceed a characteristic value. The same criterion is shown to account for the observed number of cracks which form per unit length of an exposed edge as a function of the applied stress.

(*3*) The critical stress values for various natural rubber vulcanizates suggest that a constant stored elastic energy is the appropriate criterion when rubbers of different stiffness are considered.

(*4*) The critical stored energy appears to be similar for vulcanizates of natural rubber, a butadiene-styrene copolymer (75/25 Polysar S), a butadiene-acrylonitrile copolymer (60/40 Polysar Krynac 801), butyl rubber (Polysar Butyl 400) and polychloroprene (Neoprene GN). It also appears to be largely unchanged by plasticization, by a temperature change from 20 to 50° C, and by a considerable reduction in the concentration of ozone.

(*5*) The measurements are shown to be in accord with the criterion that the propagation of a cut in an ozone atmosphere requires a characteristic energy T at the tip of the initial cut or surface flaw. For an initial sharp razor cut, the value of T obtained is of the order of 100 ergs/cm^2, only about twice as large as that expected from the energy of formation of the new surfaces.

SYNOPSIS

Experimental measurements are described of the conditions necessary for crack growth in an atmosphere containing ozone. It is proposed that a characteristic value of the tensile stress at the tip of an initial cut or surface flaw is required for growth to occur. This criterion is shown to predict the observed dependence of the applied stress required for crack growth on the length of an initial cut and on the surface smoothness of uncut test pieces. The number of cracks formed in an exposed edge is also shown to be in accordance with the proposed criterion. For vulcanizates of differing stifiness, the appropriate criterion is found to be the stored elastic energy. The critical value is shown to be similar for a number of different polymers, and largely unchanged by plasticization, a change in temperature from 20° C to 50° C, and alteration in the concentration of ozone. For initial flaws consisting of sharp razor cuts, the energy required for cut propagation is found to be about 60 ergs/cm^2 of newly formed surface.

ACKNOWLEDGMENTS

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EFFECTS OF TYPE OF RUBBER, TEMPERATURE, AND DEGREE OF CROSSLINKING ON THE FRICTION PROPERTIES OF ELASTOMERS

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The results of studies on the dependence of the frictional action of rubbers on various factors[1–10] has established that the dry friction of rubbers is unique and has a mechanism differing from that of solid bodies.

It has been shown experimentally by Schallamach[3] and theoretically by one of the authors[6] that the manner in which the rate of slip of rubber on a solid surface depends on temperature and tangential force may be described by an expression similar to that found for other molecular-kinetic processes (viscous flow, diffusion, the elastomeric deformation of polymers, the plastic flow of monocrystals and so forth). In connection with a new view on the nature of friction of elastomeric materials, it is of interest to examine the manner in which the structure and type of rubber, the temperature and other factors influences the frictional action of rubber.

We carried out an extensive investigation of the dependence of the mechanism of the friction of rubber on smooth solid surfaces on temperature, rate of slip, weight, type of rubber and crosslink density.

The data obtained confirms the specific nature of the friction of elastomers.

METHOD OF STUDY

Two basic methods were used: the method of constant tangential force (F = a constant) and the method of constant rate of slip (v = a constant); both of which, as has been shown by Roth, Driscoll and Holt[1], give comparative results for an equilibrium process of friction.

Constant rate of slip was studied on the apparatus described below. The measurements were carried out at a small rate of slip, less than 10 mm/min, where noticeable wear and heating of the rubbing surface are absent and vibration and skipping as a result of friction are not observed.

A diagram of the tribometer is shown in Figure 1. The apparatus consists of a massive base (1) on which is placed a plate (2) of steel or other solid material with a finely polished surface (the investigations were carried out with smooth solid surfaces). On the plate is placed an aluminum platform (3) to which is fastened three cylindrical specimens of rubber. The cavities for the rubber specimens were placed at the corners of an equilateral triangle with the center of gravity coinciding with the center of the platform so that an even distribution of the normal pressure would be guaranteed for all of the surfaces in nominal contact. The specimens are inserted in such a manner that they protrude 1 mm (in our experiments changing the protruding portion of the

* Translated for Rubber Chemistry and Technology from *Vysokomolekulyarnye Soedineniya* 1, 978–989 (1959) by R. L. Dunning.

rubber specimen from 0.5 to 1.2 mm did not influence the results of the experiments). On the platform are placed weights (6) of differing magnitudes which allow the changing of the normal force from 0.05 to 3 kg/cm². The nominal area of contact for the small rubber specimens was 0.36 cm² and for the large ones, 2.34 cm².

The constant rate of slip, produced by a motor through the reducer (7), was set at 0.001 to 10 mm/min. The rate of slip is checked by the movement of the point (5), readable within an accuracy of 0.01 mm.

The frictional force is determined by adjustable spring dynamometers (8) of differing sensitivities, which are inserted between the specimen and the massive plate (9) which absorbs the small vibrations of the reducer.

In order to transform the angular velocity, being set by the motor and changed by the reducer (7), into linear velocity, on the axis of the motor and reducer is placed a thickly reinforced removable disk (10) through which the thread (11) pulls the platform with the specimens at a constant velocity. The rate of slip may be varied both by changing the gear ratio of the reducer and the diameter of the removable disks.

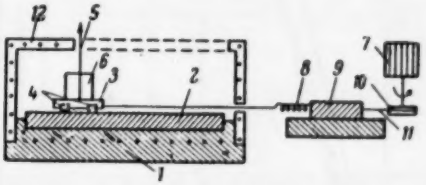

FIG. 1.—Main diagram of the tribometer for measuring the force of friction at small slip rates (explained in the text).

In order to determine the magnitude of the frictional force it is not necessary to introduce a correction for friction in the apparatus because no part of the apparatus that has friction is between the specimens and the dynamometer.

The base of the apparatus with the plate (2) and the platform (3) with the specimens are enclosed in a thermostatic chamber (12) with an electric heater.

Unfilled compounds of various rubbers were investigated, but the most detailed data were obtained for compounds of natural rubber. The specimens were vulcanized in the same press, consequently they had exactly the same rubbing surface.

It is well known that preliminary grinding of the rubber specimens influences the results of the experiments. In our experiments it was found that preliminary grinding of the rubber does not influence equilibrium friction. This indicates that the process of equilibrium friction is connected mainly with grinding, the action of which changes the active area of contact during slip to the point where a constant value of S_ϕ is established.

It is well known that the time of previous contact also influences the process of friction of rubber. Our work (Figure 2) shows that the time of previous contact only influences nonequilibrium friction. Equilibrium friction does not depend on the time of previous contact.

THE THEORY OF FRICTION OF CROSSLINKED ELASTOMERS

By examining a molecular model of friction we emerge with a model of a crosslinked elastomer which consists of flexible linear molecules connected in a

three dimensional network and existing in rapid thermal movement. Under the action of thermal motion the chains continuously change their configuration.

As a consequence of the low intramolecular barriers and the small intermolecular strength, the rubber chain segments go from one equilibrium position to another with great frequency. The residence time, τ for a chain segment of rubber in the temporary equilibrium position[11,12] is equal to about 10^{-5}–10^{-6} seconds at 300° K, which, in the formula $\tau = \tau_0 \exp(U/KT)$ at $\tau \cong 10^{-12}$, correlates to a value for the energy barrier of $U = 8 - 10$ kcal/mole. This quantity is near to the energy of activation of viscous flow of low-molecular weight liquids.

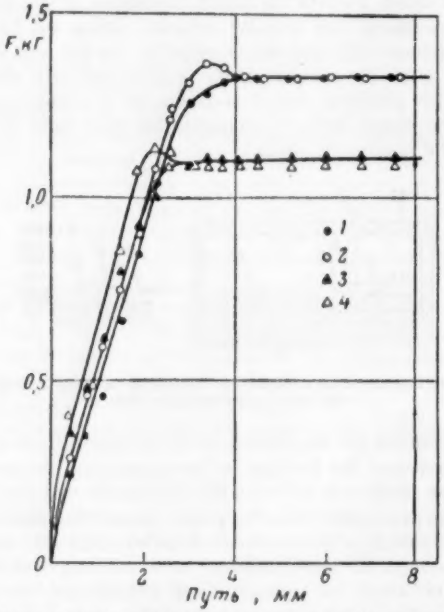

FIG. 2.—The dependence of the force of friction of soft natural rubber compounds on slip distance at two times of preliminary contact. *1, 3* are 5 min. and *2, 4* are 20 hours preliminary contact. *1, 2* are on smooth steel and *3, 4* are on rough steel.

On contact of the polymer with a solid body, parts of the polymer chains join with the latter. The number of such interactions is proportional to the effective area of contact. For there to be pure surface friction it is necessary that the adhesive strength between the rubber chains and the solid body be less stable than the chemical crosslinks and primary valence bonds. If this condition is not maintained this surface friction will either be masked by viscous flow in the bulk of the material (unvulcanized rubber, linear polymers, rubber compounds and so forth) or be absent altogether; for example, the presence of stable chemical bonds of adhesion from the hot bonding of rubber to metal or other processes that lead to welding of the surfaces.

The friction of crosslinked polymers on solid surfaces satisfies this condition. For example, vulcanized rubbers have stable crosslinks characterized by an energy of activation from various sources of 30 to 60 kcal/mole. Schallamach[3]

found that the energy of activation for the friction of rubber on glass is near 20 kcal/mole. This indicates that the adhesive bonding of the rubber with the solid body is less stable than the crosslinks of the rubber. This conclusion was confirmed in our experiments.

Each chain remains in contact with the surface for a definite length of time and then executes a jump into a new place of contact, overcoming the molecular adhesive force with the solid surface. All chains participate in the jumps during which, as a result of their flexibility, other sections of the chains are able to form a new contact with the solid surface.

Such a type of thermal movement of the chains on the surface is possible if the mobility of the chains in the bulk is many times greater than the mobility of the chain contacts with the solid surface. A comparison of the energy of activation for rubber friction ($\cong$ 20 kcal/mole) and for the thermal movement of the chain segments ($\cong$ 10 kcal/mole) shows that this condition is met.

If the tangential force is equal to zero the chains are in an unstressed condition and have an equal probability of jumping in all directions; if it is not zero, the probability is greatest in the direction of the tangential force and least in the opposite direction. Under equilibrium slip the tangential force is equally directed exactly in a direction opposite to that of the force of friction.

Accordingly[6], the rate slip of rubber on a smooth solid surface during an equilibrium process of friction is described by the formula:

$$v = \frac{\lambda}{\tau_0} e^{-U/KT} I_1\left(\frac{\gamma F}{KT}\right) \tag{1}$$

where F is the tangential force; T is the absolute temperature; U is the activation energy, which is dependent on the molecular adhesive strength with the solid surface; λ is the mean length of a chain jump, the probable value of which lies between the radius of action of intermolecular forces (10^{-7} cm) and the mean square chain length (5×10^{-7} cm). The constant $\gamma = \lambda/2N_r$ where N_r, being dependent on the normal weight, is the number of chains that are in contact with the solid surface; I_1 is the so called Bessel conversion function of the first rank and the first order[7].

In the case $z = \gamma F/kT \gg 1$, which, as will be further evident, occurs in all of the observed cases, Formula (1) may be expressed to a good approximation by

$$v = Be^{-(U-\gamma F)/KT} \tag{2}$$

where the coefficient γ and $B = \frac{\lambda}{\tau_0}\sqrt{\frac{KT}{2\pi\gamma F}}$ have a definite physical significance, with which the slight dependence of the second coefficient on F and T permits the practical calculation of its constant[1]. The value of the coefficient B is close to the velocity of sound in rubber below the glass transition temperature (1000 meters/second). In this case Formula (2) agrees with the empirical formula of Schallamach[3].

The theory is not applicable: 1) with the presence of chemical processes between the rubber and the substrate; 2) at temperatures below the glass transition temperature; 3) in friction on rough solid surfaces where it is necessary to take into account implantation of the rubber and the mechanical hooking against the microprotrusions of the solid body.

The influence of the normal weight on friction consists of a change in N_r

from the normal pressure. The number of chains N_r is proportional to the active area of contact S_ϕ. It is well known[13] that the calculation of the friction of rubber may be confined to a simple single membered relationship

$$F = cS_\phi \tag{3}$$

following from formula (1), where S_ϕ is the active area of contact; c is a constant equal to the resistance of the rubber to shear, relative to the solid surface, and calculated per unit of active surface in kg/cm².

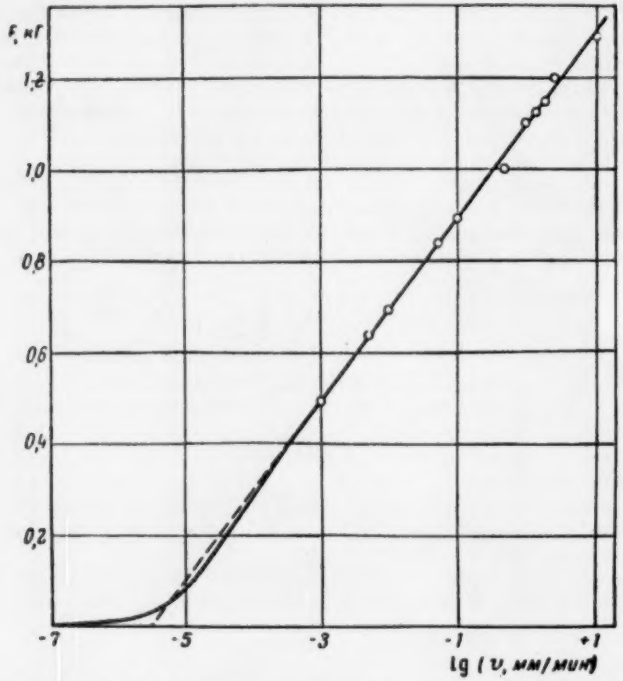

FIG. 3.—The properties of the friction of a natural rubber compound with a modulus of 9.8 kg/cm² on polished steel at 30°, with a load of 0.3 kg/cm² and $S_a = 2.34$ cm². Solid line—theoretical; broken line—experimental data.

THE RESULTS OF THE MEASUREMENTS

Since we used the method of constant rate of slip, all of our graphs treat the force of friction as a function of the rate of slip. All of our data pertain to equilibrium friction on smooth solid surfaces.

The influence of the rate of slip.—Data are cited on the friction of a natural rubber compound on a steel surface of a grade of fineness[13,14].

In Figure 3 is presented one of the characteristic curves of friction (a natural rubber compound with a modulus $E_\infty = 9.8$ kg/cm²), describing the relationship between the force of friction and the logarithm of the rate of slip, which correlates with the condition $z \gg 1$, under which the approximate Formula (2) may

be used. For example, at a rate of 1 mm per minute and a frictional force of 0.5 kg, $z = 6$. The nonfulfillment of this condition might be expected only at velocities less than 0.001 mm/minute which is not attained under industrial conditions.

The data in Figure 3 refers to the friction of rubber on steel with an area of normal contact $S_a = 2.34$ cm^2. The solid curve comes from Formula (1) with the values of the constants as follows: $\lambda = 5 \times 10^{-7}$ cm; the energy of activation $U = 18.5$ kcal/mole; and the number of chains $N_r = 4.9 \times 10^{11}$ (at all areas of normal contact). The determination of the energy of activation and the number of chains from plotting F against $\ln v$ in Formula (1) or (2) from the experimental data gives concurring results. With these coordinates straight lines are found for all of the rubbers studied by us.

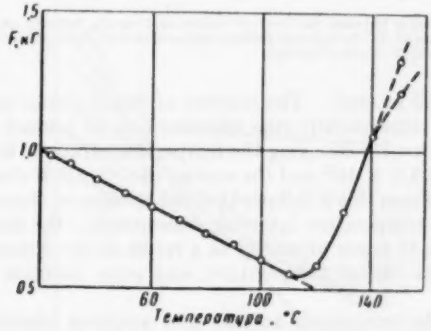

FIG. 4.—Temperature dependence of the force of friction of a compound with a modulus of 31 kg/cm^2 on polished steel at a slip velocity of 2.8 mm/min and a load of 0.3 kg/cm^2.

Analogous data were obtained for friction on glass and other solid substrates. The type of solid substrate has an influence on the magnitude of the energy of activation, which with this rubber ($E_\infty = 9.8$ kg/cm^2) equals 18.5 kcal/mole on steel, 21 kcal/mole on glass and 24.5 kcal/mole on ebonite.

Because we became further convinced that the constants U and N_r are dependent on the temperature, the load and the structure of the rubber, in the following, the determination of these constants was derived from the dependence of F on $\ln v$.

Influence of temperature.—In Figure 4 is presented the dependence of the force of friction of a natural rubber compound with a modulus $E_\infty = 31$ kg/cm^2 on steel. An analogous relationship was obtained for other compounds. The conditions of the experiment corresponds to $z \gg 1$, therefore this relation may be described by the formula:

$$F = \frac{U}{\gamma} - \frac{kT}{\gamma} \ln \frac{B}{v}. \tag{4}$$

The curve describing the dependence of the force of friction on temperature consists of two sharply different sections. For example, up to 110° the relationship is described by a straight line while at higher temperatures, it becomes an ascending curve.

From the dependence of F on $\ln v$ the number of chains and the activation energy was determined by us for this compound at various temperatures and a

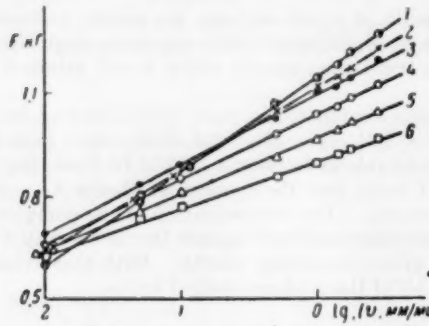

FIG. 5.—The relationship between the force of friction and log slip velocity on steel with a load of 0.3 kg/cm² and a temperature of 30° for natural rubber compounds with the equilibrium moduli: *1*—3.4; *2*—6.4; *3*—9.8; *4*—18.1; *5*—23.2; *6*—31.0 kg/cm².

constant load of 0.3 kg/cm². The number of chains found in contact with the steel surface and, consequently, the effective area of contact is practically unchanged up to 100°. By changing the temperature from 20 to 100°, N_r changes from 3.2×10^{11} to 3.5×10^{11} and the energy of activation changes from 20.8 to 18.8 kcal/mole. From this it follows that the number of chains practically does not change in this temperature interval, consequently, the decrease in the force of friction (Figure 4) arises primarily as a result of the dependence of the constant c in Formula (3) on temperature, and some decrease in the energy of activation.

Above 110° the compound softens and acquires viscous-flow properties which leads to a sharp rise in the effective area of contact. As a result the force of friction grows. Above 140° there is observed skipping under friction (the fork in the curve) for this compound.

The data presented indicate that the friction of elastomers over a wide interval of slip velocity and temperature is in good agreement with theory, where the condition $z \gg 1$ is met over all ranges of change of these parameters.

The influence of a densely crosslinked structure and the equilibrium modulus of the rubber.—In Figure 5 is presented the dependence of the force of friction on the slip rate and in Figure 6, the dependence of the force of friction on temperature for natural rubber compounds with differing values of equilibrium modulus, which is an indication of the crosslink density (Table I).

High and low modulus compounds (Figure 5) gave a clear linear relation-

TABLE I

INFLUENCE OF EQUILIBRIUM MODULUS OF NATURAL RUBBER COMPOUNDS ON THE ENERGY OF ACTIVATION AND EFFECTIVE AREA OF CONTACT[a]

E_∞, kg/cm²	λ, A	U, kcal/mole	$N_r \times 10^{-11}$ cm^{-2}	$N^1 \times 10^{-11}$ cm^{-2}	S_ϕ, %
3.4	105	17.1	6.12	0.55	11.1
6.4	66	17.4	3.46	1.05	3.30
9.8	48	18.5	2.10	1.6	1.31
18.1	30	18.7	1.11	3.0	0.37
23.2	25	18.9	0.86	3.8	0.23
31.0	20	19.9	0.51	5.1	0.10

[a] The data refer to a normal load of 0.3 kg/cm² at a temperature of 30°. The area of nominal contact, $S_n = 2.34$ cm².

ship. At temperatures up to 100°, the high modulus compounds are lineas but the low modulus compounds deviate from linearity; the lower the modulur of the compound (Figure 6), the earlier the deviation. This is apparently connected with the fact that the low modulus compounds go into the soft state earlier.

It is characteristic that the lower the modulus the greater the slope of the straight portion of the curve. This may be explained by an increase in the effective area of contact and, consequently, a decrease in the constant γ.

For the calculation of U and N_r the fact that λ depends on the dimensions of the network chains of the rubber was taken into account. In Table I is presented the values of these constants (it was assumed that λ is equal to the mean square length of the chains).

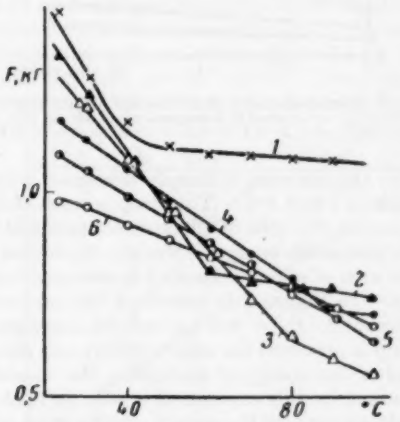

FIG. 6.—The temperature dependence of the force of friction on steel with a load of 0.3 kg/cm² and a slip velocity of 2.8 mm/min for natural rubber compounds with the equilibrium moduli: *1*—3.4; *2*—6.4; *3*—9.8; *4*—18.1; *5*—23.2; *6*—31.0 kg/cm².

The energy of activation depends on the crosslink density, although weakly, probably because the increase in the amount of bound sulfur leads to an increase in the number of polar interactions arising from the partially formed chemically bound nonbridging sulfur. By changing the equilibrium modulus from 3.4 to 31.0 kg/cm² the number of chains found in contact with the solid surface (normal load 0.3 kg/cm²) changes from 6.1×10^{11} to 0.5×10^{11} (the number of chains refers to a square centimeter of normal contact area). This number of chains differs from the total number of chains occurring in a square centimeter of rubber surface.

The statistical theory of deformation of crosslinked polymers[14] allows the approximate estimation of N number of chains per cubic centimeter from the values of the equilibrium modulus and, consequently, the number of chains $N^{\frac{1}{3}}$, found in a square centimeter of surface. This limit to the number of chains which are able to enter into contact with the solid surface is realized under a sufficiently large load. For instance, at the higher values of the modulus $N^{\frac{1}{3}}$ changes from 5.5×10^{12} to 5×10^{13} cm^{-2}. The ratio of the number of chains N_r found in contact with the surface to the number $N^{\frac{1}{3}}$ gives the ratio of the effective area of contact to the nominal area of contact. The effective area of

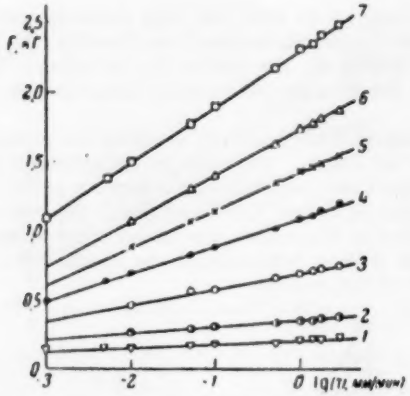

FIG. 7.—The relationship between the force of friction and log slip velocity of natural rubber compounds with a modulus of 9.8 kg/cm² on steel at a temperature of 30°, an area of nominal contact of 2.34 cm² and various loads: *1*—0.05; *2*—0.1; *3*—0.2; *4*—0.3; *5*—0.45; *6*—0.6; 7—0.8 kg/cm².

contact calculated in this manner is sharply decreased with an increase in the modulus; in our work 11.1 to 0.1%. This drop is connected with the existence of a relationship between the area of effective contact and the hardness of the rubber. Thus, the activation energy is weakly dependent on the modulus of the rubber while the area of effective contact is strongly dependent.

Influence of load.—In Figure 7 is presented the properties of friction of a natural rubber compound (E_∞ = 9.8 kg/cm²) on steel under different loads. A similar relationship is observed for other rubbers and other substrates. The influence of the load on the energy of activation, the number of chains and the area of effective contact for this compound is seen in Table II.

An unexpected dependence of the energy of activation on the load is evident and, in addition, falls rather than increases as would follow from the general considerations about the influence of load on the strength of adhesion. The understanding of this fact is further complicated because by changing the nominal pressure from 0.05 to 3 kg/cm² the effective pressure (load per unit effective area of contact) practically does not change, being approximately equal to 27 kg/cm². Thus, under a small load the formation of the area of

TABLE II

INFLUENCE OF LOAD ON THE ENERGY OF ACTIVATION AND THE AREA OF EFFECTIVE CONTACT OF NATURAL RUBBER COMPOUNDS WITH A MODULUS OF 9.8 KG/CM² UNDER FRICTION ON STEEL (30°)

S_a, cm²	p, kg/cm²	U, kcal/mole	$N_r \times 10^{-21}$, cm²	S_ϕ, %
2.34	0.05	21.0	0.3	0.
2.34	0.10	20.9	0.5	0.3
2.34	0.20	19.0	1.3	0.8
2.34	0.30	18.5	2.1	1.3
2.34	0.45	18.2	2.9	1.8
2.34	0.60	18.3	3.4	2.1
2.34	0.80	18.8	4.3	2.7
0.36	0.80	18.8	5.0	3.1
0.36	2.0	17.2	12.8	8.0
0.36	3.0	17.0	17.5	11.0

effective contact occurs in the presence of a constant and small effective pressure; it follows that in our experiments the load is unable to exert an influence on the force of adhesion and the activation energy. The effective area of contact in this range of loads changes from 0.2 to 11%. The numerical values of the effective area of contact, calculated from other experiments[12] is in agreement to an order of magnitude, with those presented by us. This concurrence is not necessary, however, to give a particular value because the values of S_ϕ that were calculated by us are dependent on some arbitrariness in the selection of the constant λ, the probable value of which lies between the radius of action of the intermolecular forces (10^{-7} cm) and the mean square length of the chains (5×10^{-7} cm), and in the determination of the number of chains from the equilibrium modulus.

In the interval of loads studied, the number of chains N_r (i.e., the effective area of contact) is observed to be a linear function of the normal pressure. For a natural rubber compound with a modulus $E_\infty = 9.8$ kg/cm^2 at a slip velocity of 1 mm/minute the constant $c = 36$ kg/cm^2. Over the range of velocities from 0.001 to 3 mm/minute this constant lies between 20 and 30 kg/cm^2.

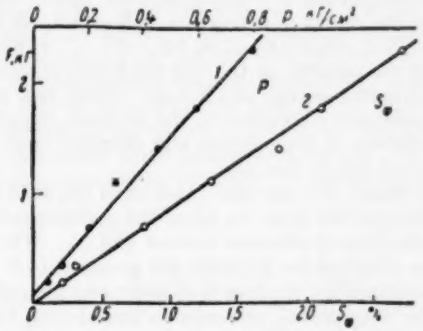

FIG. 8.—The dependence the force of friction of natural rubber compounds (modulus $E_\infty = 9.8$ kg/cm^2 slip velocity 1 mm/min) on steel on the normal load (1) and the area of effective contact (2).

The presented values for the constant are in agreement with the data obtained by Lavrent'ev under loads[13].

It may be seen in Figure 8 that the force of friction is a linear function of the area of effective contact, confirming the accuracy of Formula (3). In the same figure is shown the relationship between the force of friction and the normal pressure. This relationship is described by Coulomb's law $F = 0.1 + 2.9p$.

The influence of the type of polymer and the solid substrate.—In Figure 9 is shown the properties of the friction of various elastomers with identical cross-link densities on steel.

In Figure 10 is shown the properties of friction for natural rubber compounds on steel, glass, ebonite and a compound of SKS-30 (SBR).

From this data it can be seen that, independently of the rubbing pairs, the friction of elastomers in the range of velocities studies follows the formula of Schallamach.

If the compounds being studied are based on the same rubber, changing the modulus of elasticity, the temperature, and the load only slightly alters the energy of activation. A more pronounced change occurs upon going to another

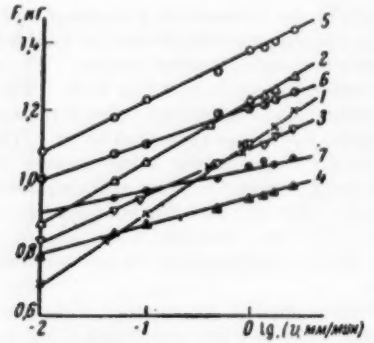

FIG. 9.—The relationship between the force of friction and log slip velocity on steel of various polymers with a modulus E_{300} = 9.8 kg/cm² (p = 0.3 kg/cm², T = 30°): *1*—NR; *2*—SKBM; *3*—SKS-10; *4*—SKS-30; *5*—SKN-18; *6*—SKN-26; *7*—SKN-40.

type of rubber. Compounds of various rubbers paired with steel gave the following values for the energy of activation: NR—18.5; SKBM—20.4; SKS—10—27.2; SKS-30—27.2; SKN-18—23.8; SKN-26—27.9; SKN-40—32.2 kcal/mole. The greater the polarity or the less the freeze resistance of the rubber the greater the activation energy of friction. From this it follows that the stronger the intermolecular interaction in the polymer, the greater the stability of the molecular adhesion of the polymer and the solid body. The butadiene-styrene rubbers do not follow this rule.

The number of chains, N_r, was calculated from the data in Figure 9. The equilibrium modulus was the same for all of the polymers although differences were apparent in the area of effective contact and N_r. The smallest value of N_r (1.7×10^{11}) was obtained for SKN-40, the greatest, (4.9×10^{11}) for NR.

This may be explained by the fact that polar and nonpolar rubbers, which have identical three dimensional networks formed during vulcanization, have different values for the non-equilibrium modulus (static modulus): the greater the static modulus, the stiffer the compound, the smaller the effective area of

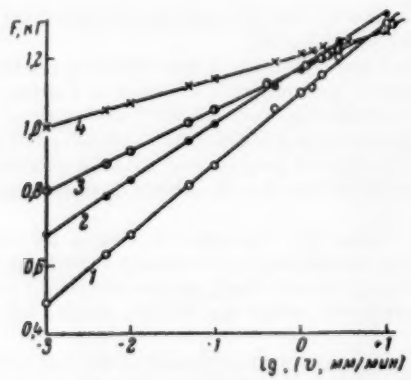

FIG. 10.—The properties of friction of the same compound as that in Fig. 3 on various solid substrates; *1*—steel; *2*—glass; *3*—ebonite; *4*—a filled SKS-30 compound.

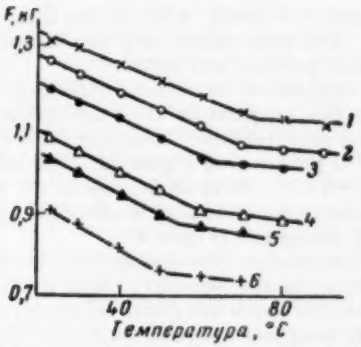

FIG. 11.—The temperature dependence of the force of friction of compounds of SKBM ($E_\infty = 9.8$ kg/cm², $p = 0.3$ kg/cm²) on steel at the slip velocities: *1*—2.8; *2*—1.0; *3*—0.5; *4*—0.11; *5*—0.5 (0.05 ?); *6*—0.01 mm/min.

contact. For example, from the literature[15] the dynamic modulus E' for SKN-40 is given as 48.0 kg/cm² while that for NR is given as 12.7 kg/cm² at identical values of E_∞ = 9.0 kg/cm²; from our data the static one minute moduli for the same rubbers are equal to 15.0 and 10.5 kg/cm² respectively.

An unexpected finding was that the activation energy of friction of rubber on rubber (Figure 10) proved to be high (35 kcal/mole). It is possible that the cause of this is the ability of the chains of the rubber to diffuse into the surface layer at the place of contact if the substrate is rubber. If the portion of the chains found intermingled with the other rubber surface is a significantly larger

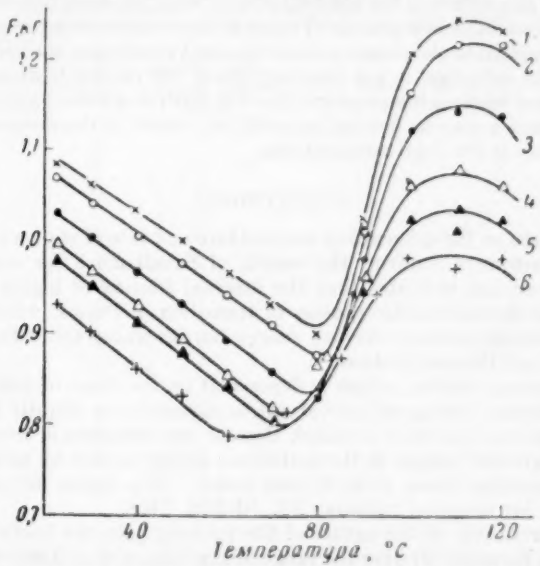

FIG. 12.—The temperature dependence of the force of friction of compounds of SKN-40 ($E_\infty = 9.8$ kg/cm², $p = 0.3$ kg/cm²) on steel at the slip velocities: *1*—2.8; *2*—10.; *3*—0.5; *4*—0.1; *5*—0.05; *6*—0.01 mm/min.

number of the segments, the energy of extracting them must be substantially above 10 kcal/mole. This same reason, as is well known, explains the stability of the adhesion between polymer and polymer[16].

The temperature dependence for various rubbers and substrates are similar below 60–70°; above this temperature the relationship has a different character for nonpolar and polar rubbers. Nonpolar rubber is shown in Figure 11 and the polar rubber is presented in Figure 12. Natural rubber behaves in a manner analogous to SKBM. With an increase in the modulus, the inflection in the temperature relationship gradually is smoothed out and at a modulus of E_∞ = 31 kcal/mole it disappears (Figure 4).

These particular temperature relationships may be explained with existing ideas about the influence of the secondary bonds in the network of the vulcanizates. These unstable bonds are destroyed at elevated temperatures and practically completely disappear above 70–80°.

The comparative increase in the force of friction above these temperatures (slight for nonpolar rubbers and large for polar ones) is, apparently, more or less connected with a sharp decrease in the static modulus following the destruction of the secondary bonds. As a result of the increase in the area of effective contact the force of friction grows.

The greatest effect is observed with SKN-40 in which the formation of secondary bonds is a result of polar bonds, the number of which is greater in that rubber than in SKN-26 and SKN-18. From Figures 11 and 12 it can be seen that the earlier the deviation from linearity, the smaller the rate of slip. This is connected with the kinetic nature of the nonequilibrium modulus. A confirmation of the previous explanation is found in the fact that the inflections in the temperature cruves occur at approximately the same temperature independently of the nature of the solid substrate (with the exception of glass).

For high modulus compounds (Figure 4) the relative number of secondary bonds as compared to the primary ones (chemical crosslinks) is extremely small. Therefore, the inflection is not observed above 70° on the temperature curve up to the point where a temperature (for NR 120°) is attained above which the rubber becomes a viscous flowing material as a result of the destruction of the primary bonds at the high temperatures.

CONCLUSIONS

1. The data on the influence of temperature and rate of slip on the frictional action of elastomers confirms the results of Schallamach for compounds of natural rubber and indicates that the external friction of highly elastic materials is a molecular-kinetic process of transition of chains, which adhere to the other rubbing surface, over an energy barrier under the action of an external force and thermal motion.

2. The energy barrier, which is dependent on the force of adhesion of the rubbing materials (energy of activation), is changed only slightly by changing the temperature, load and crosslink density for compounds from the same rubber. A greater change in the activation energy occurs by going from one polymer to another (from 18 to 32 kcal/mole). It is higher for polar rubbers (SKN) than for nonpolar rubbers (NR, SKBM, SKS).

3. Independently of the nature of the rubbing pair, the friction of elastomers follows Formula (2) over the range of slip velocities of 0.001–10 mm/min. In spite of the use of extremely small slip velocities, such a limit was not reached which might be attributed to the existence of actual static friction with the

highly elastic materials. On the contrary, the drop in the coefficient of friction with decreased rate of slip became sharper the smaller the rate. For all elastomers there is observered a drop in the force of friction up to 60–80°. Above this region is an anomolous portion of the curve, the more sharply expressed, the greater the polarity of the rubber. The anomolous change in the force of friction is connected with the increase in the effective area of contact resulting from the destruction of the secondary bonds in the three dimensional network and a decrease in the static modulus of the compound.

5. High modulus compounds give a linear relationship for the force of friction up to 100–120° while low modulus compounds have a deviation in their linearity which appears, the earlier, the lower the equilibrium modulus. The slope of the linear portion of these compounds is greater than that of the lower modulus compounds which is connected with the increase in the effective area of contact at the transition from a hard to a soft compound.

6. At small normal loads (to 3 kg/cm^2) the properties of the law of friction may be described by Coulomb's law. The force of friction is a linear function of the effective area of contact.

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THE NATURE OF AN ADHESION BOND BETWEEN TWO HIGH-MOLECULAR WEIGHT COMPOUNDS *

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In our earlier papers[1] the view was put forward that in a number of cases an adhesion bond is formed by electrostatic interaction of the layers of an electric double layer formed at the interface during the formation of an elastic film of polymer from a solution applied to the substrate surface.

Various authors[2] have repeatedly put forward views on the role of diffusion processes in the formation of adhesion and autohesion bonds. It is stressed in G. L. Slonimskii's paper, presented at the Conference on the Strength of Bonds Between Components of Rubber—Fabric Articles (Goskhimizdat, 1956, p. 11), that the electrical theory of adhesion allegedly does not take into account the possible formation of a transition layer, conferring a cohesive character to the separation of the adhesive. In reality, in the paper by B. V. Deryagin, S. K. Zherebkov, and A. M. Medvedeva[3] presented at the Conference on Adhesion held in the Institute of Physical Chemistry, Academy of Sciences USSR in May 1955, it was not only stated that such cases are possible, but it was rigorously proved that such cases arise if the polymers are compatible, and the adhesion may be the result of diffusion of the chains of the contacting objects rather than of the formation of an electric double layer. If the separation is purely adhesive, the electrical theory of adhesion is fully applicable.

The purpose of the present investigation was to carry out an experimental study of the formation of an adhesion bond between two high polymers and to determine the relative roles of electrical and diffusion processes in adhesion.

The electron-emission effects observed by one of the present authors (jointly with Karasev and Deryagin[4]) when adhesion bonds are destroyed in such systems as polymer-glass, polymer-metal, and polymer-polymer, and the electron emission from a freshly detached polymer surface, make it possible to analyze, in each individual case, the nature of the processes which occur when the adhesion bond between two polymer specimens is broken. Some information on the nature of the bonds is also obtainable from microscopical investigations of cross sections of joints, and from adhesiograms.

We showed previously[5] that the plot of the logarithm of the work of separation A against the logarithm of the separation rate v forms an adhesiogram with three linear regions (Figure 1a); these were explained as follows: in Region III, parallel to the abscissa axis, when separation is rapid, the observed effects conform to Paschen's law of gas discharge. Luminescence is observed in this region during separation if the experiment is performed under moderate vacuum, and electron emission under high vacuum. In Region II, where the relationship $A = f(v)$ is most pronounced, the charges of the electric double layer become neutralized during separation of the joint, by surface leakage. The slower the process of separation (in which the capacitor layers are drawn

* Reprinted from *Colloid Journal* **20**, 55–62 (1958); a translation by Consultants Bureau, Inc. of *Kolloid. Zhur.* **20**, 59–66 (1958).

apart), the more important the process of charge leakage along the boundary of the detaching film becomes. In some cases (as in the system nitrocellulose-glass), if the separation is very slow, the charges can leak away completely, and then A become independent of v in Region I of the adhesiogram, parallel to the abscissa axis, and the order of magnitude of A corresponds to equilibrium adhesion, described by the Dupre-Yound equation and caused by intermolecular forces.

In other cases the value of A in Region I may be greater by several orders of magnitude, but Region I itself remains parallel to the abscissa axis. Evidently charge leakage in this region is a considerably slower process than separation of the capacitor plates. Because of all this, region I for polymers of this kind, in which adhesion is determined to a considerable extent by forces of electrostatic attraction, was given the name of the pseudoequilibrium region by Deryagin[5].

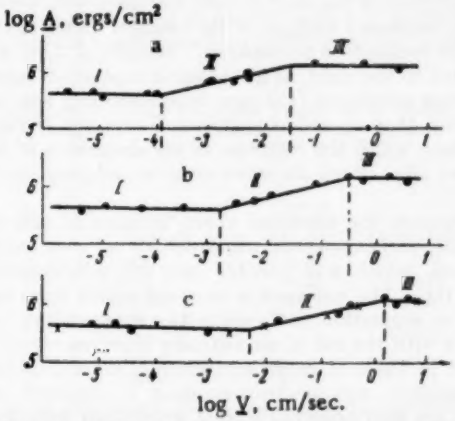

FIG. 1.—Effect of specimen width on the form of the adhesiogram for chlorinated polyvinyl chloride—rubber (SKB): a) 1 mm; b) 3 mm; c) 5 and 10 mm.

In the present investigation, the roller adhesiometer of Krotova's design was used to obtain adhesiograms for a number of polymers (BF-type glue, polyurethane, polyamides, vinyl polymers, rubbers and guttapercha, cellulose esters, etc). The adhesiograms of some combinations of these polymers with glass, metals, and rubbers based on sodium butadiene and acrylonitrile polymers, show the three well-defined regions discussed above. In other cases (the majority) Region III is absent. It is possible that such a region does exist, but is situated in the range of high rates, where experimental determination is difficult. Time invervals less than 0.01 second could not be measured in our experiments.

Since the surface electrification density σ can be determined only in the applicability range of Paschen's law, it is extremely important to determine the factors which influence the form of the adhesiogram and the position of the inflection points on it. Our experiments show that one such factor is the width of the specimen. Its effect is such that when the width of the specimen is altered from 1 to 5 mm the middle Region II of the adhesiogram is displaced to the right; all the other characteristics of the adhesiogram (levels of Regions I and III, the slope of the middle region) remain unchanged (Figure 1a, b, and

TABLE I

EFFECT OF SPECIMEN WIDTH ON THE DISPLACEMENT OF THE MIDDLE REGION OF THE ADHESIOGRAM

Specimen width, mm	Separation rates in cm/sec. corresponding to the middle region of the adhesiogram
1	$1.26 \cdot 10^{-4}$–$2.9 \cdot 10^{-2}$
3	$1.58 \cdot 10^{-3}$–$0.25 \cdot 10^{-2}$
5	$5.63 \cdot 10^{-3}$–$1.58 \cdot 10^{-2}$
10	$5.63 \cdot 10^{-3}$–$1.58 \cdot 10^{-2}$

c). The displacement of the middle region is shown by the data in Table I for the chlorinated polyvinyl chloride—sodium butadiene rubber system.

It is clear from the data in Table I that specimen width has an influence up to a definite limit (5 mm) only. This may be explained as follows. Dispersion of the lines of force of the electric field increases with decreasing specimen width, leading to decreased leakage of the charges under the influence of the field by the surface conduction mechanism. Because of this, in wide specimens Region II is shifted to the right, as at the same separation rates the leakage of charges from narrow specimens (1–3 mm) is considerably less, and the adhesion is therefore greater, than in wide specimens (5 mm and over). With further increase of specimen width the influence of the dispersion of the lines of force becomes small and edge effects therefore cease to influence the form of the adhesiogram.

In our experiments the electrical characteristics of adhesion (potentials, potential gradients, surface electrification density σ) were calculated from the gas discharge laws, which was possible only for adhesiograms with clearly defined Regions III. The values of σ were calculated from the values of the maximum work of separation (adhesion) A_0 corresponding to the maximum separation rates v with the aid of an auxiliary Paschen curve (Table II). In all the cases given in Table II, rapid separation in air and in moderate vacuum results in luminescence, and electron emission is observed in high vacuum. Electrical effects are also observed during separation with high-strength adhesives (BF-type glue, polyurethanes, polyamides), but in view of the absence of Region III in the adhesiograms it is not possible to calculate σ, and only the lower limit of the values of σ can be estimated, although there is no doubt about the electrostatic nature of the adhesion bonds in such cases.

The maximum velocities of the electrons emitted during the separation may give an idea of the potential difference of the double layer after its separation,

TABLE II

CHARACTERISTICS OF THE ADHESION OF POLYMERS TO VARIOUS SURFACES*

Polymer	Substrate	$A \cdot 10^{-4}$ (erg/cm², pseudoequilibrium) at $v = 10^{-3}$ cm/sec.	$A_0 \cdot 10^{-4}$ (erg/cm², limiting) at $v = 1$ cm/sec.	Discharge potential in volts $\cdot 10^{-2}$	Discharge interval μ	$\sigma \cdot 10^6$ in e.u./cm²
Guttapercha	Glass	1.3	1.78	6.3	1.00	1.67
Guttapercha	Gelatin	2.9	3.55	9.0	0.96	2.52
Guttapercha	Steel	0.56	4.00	9.3	0.94	2.64
Nitrocellulose	SKB rubber with kaolin filler	10.1	3.16	8.6	0.95	2.42
Chlorinated polyvinyl chloride	The same	10.1	5.63	11	0.93	3.10

* Separation of these specimens is accompanied by electron emission. The adhesiograms have three distinct regions. The values of σ were calculated from Region III, Figure 1, of the adhesiograms, in the applicability range of Paschen's law.

as these electrons are dispersed by the fields which exist in the gap between the separated surfaces. After σ has been determined from the experimental data and Paschen's curve, the potential difference and the value of σ can be used to calculate the work of adhesion A, and the result may be compared with the value of A determined experimentally by a mechanical method (Table III).

It is seen in Table III that the theoretically calculated values are in good agreement with the experimental data (apart from the chlorinated polyvinyl chloride—SKB rubber system), thus confirming the electrical theory of adhesion.

We showed earlier[6] that a polymer film after separation contains separate centers of emission. It is suggested that the adhesive film is not bound continuously to the substrate, but only to separate regions, and these emit electrons after the adhesion bond has been broken. It is to be expected that when regions of the closest and most continuous contact are separated, the emission intensity would be higher in such regions. It is well known that mechanical treatment of the substrate surface results in an increase of adhesive strength; although, this effect may have various causes, such as changes in the surface properties of

TABLE III

WORK OF SEPARATION A_0 OF POLYMER FILMS FROM VARIOUS SURFACES AND VELOCITIES OF ELECTRONS EMITTED DURING THE SEPARATION AT $p = 10^{-4}$ MM Hg*

Polymer	Substrate	Electron velocities in ev·10^{-8}	$A_0 \cdot 10^{-4}$ in ergs/cm²	
			Experimental	Calculated from electron velocity
Chlorinated polyvinyl chloride	Brass	2.45	2.45	1.04
	Glass	6.25	3.16	2.52
	Gelatin	11	31.6	28.2
	SKB rubber (kaolin filler)	25	159	53.6
Polyisobutylene	Gelatin	11	35.6	31.7

* Experiments carried out under vacuum; curves plotted for the high-rate region.

mechanically treated surfaces, or thinning of the oxide film, it is generally attributed to an increase of contact area. It was therefore of interest to find whether the emission intensity of a detached polymer film is highest at regions where the film had been in contact with a mechanically treated surface. For this, grooves were made in a metal (brass) surface by means of a file, and the surface was coated with a polymer solution. The experiments were performed in a vacuum roller adhesiometer of modified design, in which an x-ray film was placed very close to the separating polymer film and moved synchronously with it. The photographs show clearly that the electron emission was most intense at the regions of the polymer film where it was separated from the grooves in the metal (Figure 2a and c). The images are intended to show: (a) emission from regions of chlorinated polyvinyl chloride film attached to deep grooves on brass surface; (b) same, with the letter E marked on the brass; (c) lines marked on the brass; (d) emission from surface of a guttapercha film stripped from rubber filled with kaolin (no emission from regions in contact with rubber filled with carbon black); (e) same, stripped from rubber filled with carbon black and treated with H_2SO_4. [The images of Figure 2 were too unclear for reproduction. Ed.]

These experiments and the data in Table III lead to the conclusion that the magnitude of the adhesion (if it is caused by electrostatic forces) is closely

associated with the velocity of the emitted electrons on the one hand, and with the intensity of electron emission on the other. This is understandable in the light of the electrical theory of adhesion.

The influence of the chemical structure of the bonded substances on adhesion is a highly important question. By De Bruyne's empirical rule, known to specialists, a high degree of adhesion is obtained between polymers of similar polarity, i.e., polymers with polar functional groups, or between nonpolar polymers of similar structure.

Deryagin, Zherebkov, and Medvedeva[3] showed that in most cases there is a correlation between the adhesive shear strength of polymers and the similarity of their polarities. They regard this as the most convincing evidence of the role of polymer chain diffusion in the formation of adhesion bonds between polymers of similar nature.

The purpose of the present work was to analyze the nature of the adhesion bonds between different types of polymers, by disruption of the bonds (and by microscopical investigation of cross sections of the contact surfaces), in relation to the chemical structure of the bonded substances.

It was found that the systems studied can be divided into two main groups. The first group is characterized by electrical effects on disruption of the adhesion bond: luminescence in moderate vacuum, electron emission in high vacuum, and the presence of residual charges on the separated surfaces. The sign of the charge was determined with the aid of a simple radiometric circuit; the following rule was found to apply in all cases: the surface which emits electrons after separation has a negative residual charge, while the opposite surface, which does not emit electrons, has a positive residual charge.

Microscopical investigations of sections (micrographs are not shown here owing to lack of space) show the existence of a sharp boundary between the two polymers in such cases. Sometimes, when the adhesion is particularly great, the separation occurs along the polymer film. Neither electron emission nor residual charges on the separated surfaces are found in such cases. The work of separation is very large, and in such cases the work of adhesion is evidently greater than the work of cohesion. Microscopical investigations also reveal a distinct boundary. Systems of this kind are formed from components with strongly polar groups (BF-6 glue and acrylonitrile rubber, chlorinated polyvinyl chloride and rubber the surface of which was treated with concentrated H_2SO_4 and then washed).

The following case is of interest. If one of the components is SKB rubber with carbon black filler, no electron emission is observed when a film of any polymer is detached from it, although the separated surfaces carry residual charges of opposite sign. Separation of polymers from the same rubber, but filled with kaolin, results in very intense electron emission. A special substrate specimen consisting of alternating bands of rubber containing carbon black and kaolin was prepared, and a polymer film was stripped from it. Figure 2d (not reproduced in this translation) shows that emission occurs only at those regions (of the gutta-percha) which had been in contact with the rubber containing kaolin, whereas the regions in contact with the rubber containing carbon black do not emit. However, if the surface of rubber containing carbon black, heated at 120°, is treated for 3 minutes with concentrated H_2SO_4 and then washed, which leads to the formation of new polar groups in the surface, electron emission may be observed when a guttapercha film is stripped from this surface (Figure 2e, not reproduced in this translation).

It must be pointed out with reference to these results that the presence or

absence of electron emission when the polymer is detached does not in itself prove or disprove the applicability of the electrical theory of adhesion in the given instance. The sole significance of electron emission is that it can be used to estimate the potentials of the electric double layers from the velocities of the emitted electrons. At the same time, the existence of charges on the separated surfaces, representing the residual surface electrification density, which is a certain part of the initial density σ of the double layer, is an indication of the electrostatic character of the adhesion bond.

TABLE IV

CLASSIFICATION OF VARIOUS FILM—SUBSTRATE SYSTEMS BY THE NATURE OF THE ADHESION BOND

Systems and sign of residual charges in systems separated in air (+ or −) and type of separation (I = adhesive, II = cohesive and III = mixed type)	Electron emission after separation under vacuum $P = 1 \cdot 10^{-4}$ mm Hg	Work of separation at $v = 1$ cm/sec in ergs/cm$^2 \cdot 10^{-4}$
Systems of the first group		
Chlorinated polyvinyl chloride (−) Steel (+) (I)	Emission by PVC	1.04
Chlorinated polyvinyl chloride (−) Glass (+) (I)	Emission by PVC	2.52
Polyethylene (−) SKB rubber (+) (kaolin filler) (I)	Polyethylene	4.45
Polyethylene (−) SKN rubber (+) (kaolin filler) (I)	Polyethylene	5.63
Guttapercha (−) Glass (+) (I)	Guttapercha	1.78
Polyvinyl butyral (−) SKB rubber (+) (kaolin filler) (I)	Polyvinyl butyral	20.2
Chlorinated polyvinyl chloride (−) Gelatin (+) (I)	Chlorinated polyvinyl chloride	28.2
Polyamide (−) SKB rubber (+) (kaolin filler) (I)	Polyamide	30.1
Nitrocellulose (−) SKB rubber (+) (kaolin filler) (I)	Nitrocellulose	91.6
Gutta-percha (−) Steel (+) (I)	Guttapercha	39.8
BF-6 (−) SKB rubber (+) (kaolin filler) (I)	BF-6	39.8
Chlorinated polyvinyl chloride (−) Ditto (I)	Chlorinated polyvinyl chloride	56.3
Polyurethane (−) Ditto (I)	Polyurethane	63.2
Guttapercha (−) SKB rubber (with carbon black filler) treated with H_2SO_4 (+) (I)	Guttapercha	65.2
Guttapercha (−) SKN rubber (+) (kaolin filler) (I)	Guttapercha	105
Polyamide (−) Ditto (I)	Polyamide	112
Polyethylene (−) SKB rubber* (+) (containing 40% carbon black) (I)	No emission	4.45
Polyvinyl butyral (−) (I) Ditto	No emission	175.
Polyamide (−) Ditto (I)	No emission	28.4
Nitrocellulose (−) Ditto (I)	No emission	30.4
Chlorinated polyvinyl chloride (−) (I)	No emission	54.1
BF-6 (−) (I)	No emission	38.7
Polyurethane (−) Ditto (I)	No emission	62.3
Nitrocellulose SKN rubber (kaolin filler) (II)**	No emission	300
Chlorinated polyvinyl chloride (−) (II)	No emission	300
Polyurethane Ditto (II)	No emission	300
BF-6(−) SKN rubber (kaolin filler) (II)**	No emission	300
Chlorinated polyvinyl chloride (−) SKB rubber (with carbon black filler) treated with H_2SO_4 (II)**	No emission	300
Systems of the second group		
Polyethylene Polyisobutylene (III)	No emission	119
Polyethylene Paraffin wax (III)	No emission	50.4
Guttapercha Paraffin wax (III)	No emission	50.4

* No electron emission is observed on separation of polymers from this rubber with carbon black filler, although the separated surfaces carry charges of opposite sign. Electron emission occurs with lower contents of carbon black.

** Rubber separates.

Systems of the second group (Table IV), consisting of nonpolar components, are significantly different. When the components of these systems are separated, no electron emission occurs and there are no charges on the separated surfaces. Microscopical examination of sections shows the boundary to be diffuse. This shows that in systems of the second group the adhesive bonds are formed by diffusion of the polymer chains in the contact zone. It cannot be said that the adhesive bond strengths of either group of systems are higher than those of the other. However, the first group contains some "weak" specimens (for example, chlorinated polyvinyl chloride-steel, or polyethylene-rubber (see Table IV).

The reaction (pH) of the substrate is very significant in adhesion effects; this was demonstrated by our experiments on the adhesion of chlorinated polyvinyl chloride to glass.

The experimental procedure was as follows: small amounts (about ½ ml.) of H_2SO_4 or NaOH solutions of various concentrations were applied from a pipet to a glass surface (40 × 70 mm). The solution was spread uniformly over the whole surface and the excess was removed by means of filter paper at the edge of the plate. A polymer film was then applied in the usual way and its adhesion to glass was determined by means of an adhesiogram in the region of high stripping rates. Figure 3 shows the variation of the work of separation A_0 at $v = 1$ cm/sec. with the concentration of the solution applied to the glass surface.

Figure 3 shows that the maximum adhesion A_0 corresponds to the neutral region. The separated surfaces, in the region of maximum adhesion, carry residual charges: positive on the polymer film and negative on the glass. If the

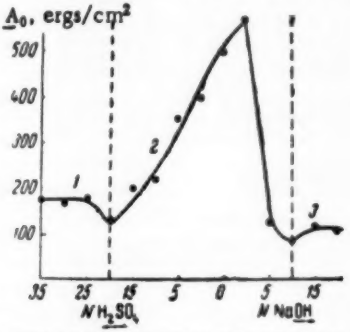

FIG. 3.—Effect of the reaction of the glass surface on its adhesion to chlorinated polyvinyl chloride: *1*) and *3*) film positively charged after separation; *2*) film negatively charged.

glass is covered with a film of acid or alkali solution of high concentration, then the polymer film in contact with it must evidently undergo chemical change, probably by surface oxidation in an acid medium in the first case, and an alkaline medium in the second.

When a polymer film is stripped from a strongly acid or strongly alkaline glass surface, there is a sharp decrease of the work of adhesion and a change in the sign of the charges on the separated surfaces. The glass surface acquires a negative charge, while the polymer surface is positively charged. Thus, the charge reversal is accompanied by sharp decreases of the work of adhesion both in the acid and in the alkaline regions, which can be attributed only to a decrease of the surface electrification density of the layers of the electric double layer in the charge reversal region.

ACKNOWLEDGMENT

The authors express their gratitude to Corresponding Member (AN SSSR) B. V. Deryagin for valuable guidance, and to V. V. Karasev for helpful advice and constant assistance in the experimental work.

SUMMARY

1. The nature of the adhesion bonds in different cases can be determined by investigations of the mechanical characteristics of adhesion, of electrical

effects observed on destruction of the bond, and microscopical investigation of the separation boundaries in various systems consisting of polymer pairs, and polymer-metal and polymer-glass systems held together by forces of adhesion.

2. The adhesion bonds between polymer and metal and polymer and glass are electrical in character, as shown by the form of the adhesiogram, the occurrence of electron emission on separation, and the existence of electric charges on the separated surfaces.

3. After separation, the polymer film continues to emit electrons and carries a negative residual charge. The substrate (glass, metal) does not emit electrons and has a positive charge.

4. The breakdown of the adhesion bond between two polar polymers of different structure, or a polar and nonpolar polymer, is accompanied by the same characteristic effects as the separation of a polymer from glass or metal. A sharp boundary is observed in microscopic specimens.

5. Determinations of the velocities of electrons emitted during separation show that breakdown of a firm adhesion bond is accompanied by emission of electrons with higher velocities than those emitted in the breakdown of a weak bond. These results are in good agreement with the electrical theory of adhesion.

6. The reaction of the substrate (glass) has a strong influence on the adhesion of a polymer (chlorinated polyvinyl chloride) to it. The maximum adhesion is found in the neutral region. The detached polymer film shows a reversal of residual charge in the strongly acid and strongly alkaline regions, accompanied by a sharp decrease of the work of adhesion; this can only be attributed to a decrease of the surface electrification density of the layers of the electric double layer in the charge reversal region.

7. Mechanical treatment of the metal surface increases the adhesion of polymers to it and intensifies electron emission from the regions of the polymer film which were attached to the treated regions of the metal surface.

8. The formation of an adhesion bond between two nonpolar polymers of similar structure is caused by diffusion processes in the contact zone. In such cases no electrical effects are observed during separation, the boundary in microscopic specimens is diffuse, and the work of separation depends relatively little on the rate of separation.

9. The systems studied can be subdivided into two groups: the adhesion bond in systems of the first group is the result of formation of an electric double layer at the boundary; in systems of the second group the adhesion bond is produced by diffusion processes at the boundary.

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THE INFLUENCE OF POLYMERS WITH CONJUGATED BOND SYSTEMS ON THE STABILITY OF POLYVINYLCHLORIDE *

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We may now consider thermal and light initiated oxidative degradation in halogen-containing carbon-based polymers to occur through a radical-chain mechanism[1]. Obviously the process is initiated by radical products of degradation in macromolecules, particularly by alkoxyl and hydroxyl radicals originating in the breakdown in the polymer of hydroperoxides[2,3]. The development of the chain process occurs with the splitting out of atoms of hydrogen and halogen, resulting in dehydrochlorination to form double bonds and breaking down of the macromolecule[1–3]. Although until recently there has been no very well-defined indication of the mechanism of formation, development, and splitting of the chains through thermal and light-oxidative degradation of polyvinylchloride (PVC) it may be asserted that the most effective inhibition of this process is possible only by using materials which have the ability to accept radicals. Naturally, the radical acceptors employed can only be those which on heating, and exposure to the presence of air will not form hydroperoxides capable of reinitiating the destructive processes.

Of major theoretical and practical interest in this connection, there have been described investigations on the effect of thermoxidative degradation in PVC, by a certain type of recently synthesized polyphenylvinylene (PPV)[4] also containing the conjugated bonds of the degradation products of some high polymers, in particular PVC.

The minor activity of such quasiradicals may be explained by the fact that they are able to react only at relatively high temperatures (>150–200°)[4]. Investigation of the electron paramagnetic resonance spectra of PPhV. and dehydrochlorinated PVC indicates that they contain, in the ground state, a great number of unpaired electrons, 10^{17}–10^{19} paramagnetic particles per gram, delocalized in conjugated links[5]. This circumstance allows the presumption that they may be highly effective inhibitors of the process of thermo-oxidative degradation of halogen-containing polymers. Experimental data, given in Table 1, confirms the validity of this assumption.

Polyphenylvinylene (I), produced by the thermal polymerization of phenylacetylene at 150° appears to be an extremely effective inhibitor of thermo-oxidative degradation of PVC. Of less inhibitory effectiveness is the infusible and insoluble copolymer (II) of phenylacetylene and *p*-diethylbenzene produced at 300°, and similarly the product III obtained by exhaustive dheydrochlorination of PVC, under vacuum at 300°.

Figure 1 gives the kinetic picture for the splitting of hydrogen chloride from PVC at 175° in the presence of various stabilizers; the curves demonstrate the great effectiveness of the inhibiting action of product I.

* Translated by J. R. Robinson from *Doklady Akad. Nauk*, SSSR. 131(3), 563–565 (1960).

TABLE 1

Stabilizer: Material	Stabilizer: No. of paramagnetic particles per gram	% of stabilizer, based on PVC	Temp. of beginning of dehydrochlorination of PVC, °C	Duration of induction period to beginning of dehydrochlorination	V, mg HCl / g PVC	$\frac{V}{V_0}\cdot 100\%$
Polyvinylchloride without stabilizer	—	—	158	7 min.	3.91	100
Polyphenylvinylene (I)	2.41×10^{17}	0.1	—	8.5	2.16	55
		1.0	158	7	1.34	34
		5.0	—	7	1.30	33
		10.0	—	5	1.43	37
Copolymer of phenylacetylene and *para* diethylbenzene (II)	4.35×10^{18}	0.1	—	6	2.54	65
		1.0	153	7	2.53	65
		10.0	—	5	3.30	84
Dehydrochlorination product of PVC (III)	2.10×10^{17}	1.0	160	9	3.07	78
		5.0	—	8	2.41	65
		10.0	—	10	3.13	80

Note: The mean integral velocity of the dehydrochlorination of PVC in the presence (V) and absence (V_0) of stabilizer was determined at 175° in a current of air and an experiment duration of 180 minutes. The relationship $\frac{V}{V_0}\cdot 100$ characterizes the variation in velocity of dehydrochlorination due to the introduction of the stabilizer.

It will be noted that on use of even larger quantities of the insoluble products, the stabilization effect is diminished. Obviously, when using these insoluble and infusible polymers with conjugated bond systems (II and III), the contact of the radicals formed in the degradation of PVC with the active centers of the polymeric stabilizer molecules is very greatly limited.

The data of Table 2 shows the inhibitory effect of polyvinylenes I and III on the breakdown of polyvinylchloride at various temperatures.

These data affirm the lessening in effective action of the polyvinylenes as temperature is increased. Product I inhibits thermal decomposition of polyvinylchloride at 185°, and does not intensify it at 195°. In contrast to I, product III accelerates the degradation of PVC at 195°. This specific action

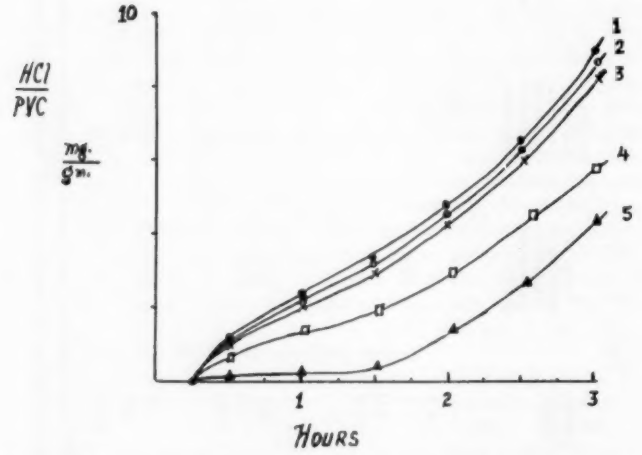

FIG. 1.—Velocity of dehydrochlorination of polyvinylchloride at 175° in an air-stream; *1*—without a stabilizer; *2*—with 1% of lead silicate; *3*—with 1% di-butyl maleate; *4*—with 1% diphenylpropane; *5*—with 1% polyphenylvinylene (I).

of product III, produced by dehydrochlorination of PVC, is obviously connected with the formation of active radicals by thermal cracking of the polymer. Such radicals may be "caged" in the network of the dehydrochlorinated polymer and there interact with oxygen to form peroxide radicals, thus initiating the decomposition of the PVC at lower temperature.

In connection with this it is of interest to report on the effect of thermal treatment of polyphenylvinylene I on its stabilizing activity. Experimental data indicate that on heating I to 300 and 400°, an intensification in the degree of conjugation is observed, which may be estimated by the deepening color of the polymer from a yellow to brown and black; with this occurs an increase in the concentration of unpaired delocalized electrons from 2.4×10^{17} to 4.2×10^{18} and 3.4×10^{19} paramagnetic particles per gram respectively[4]. Simultaneously there appears to be a partial dehydrogenation of the polymer, reflected by the hydrogen content declining from 6.12 to 5.88 and 5.16% and, obviously, creating the possibility of forming radical centers. The data of Figure 2 confirm the hypothesis on the probability of formation of action radicals which are then able to initiate the degradation of PVC. The polyphenyl-

TABLE 2

Stabilizer	% Stabilizer based on PVC	Temp. at which velocity of dehydrochlorination was determined, °C	Duration of induction period to beginning of dehydrochlorination	V, $\frac{\text{mg HCl}}{\text{1 gm. PVC}}$	$\frac{V}{V_0}\cdot 100\%$
Polyvinylchloride without stabilizer	—	175	7 min.	3.91	100
		185	6	10.0	100
		195	5	20.7	100
Polyphenylvinylene (I)	1.0	175	7	1.34	34
	1.0	185	5	6.30	63
	5.0	185	6	6.20	62
	10.0	185	7	6.17	62
	1.0	195	3	19.0	92
	5.0	195	3	20.0	96
	10.0	195	3	20.8	100
Dehydrochlorination product of polyvinylchloride (III)	1.0	175	9	3.07	78
	1.0	185	8	7.8	78
	5.0	185	6	6.4	64
	10.0	185	7	9.0	90
	1.0	195	6	27.0	130
	5.0	195	5	20.7	100
	10.0	195	6	31.2	151

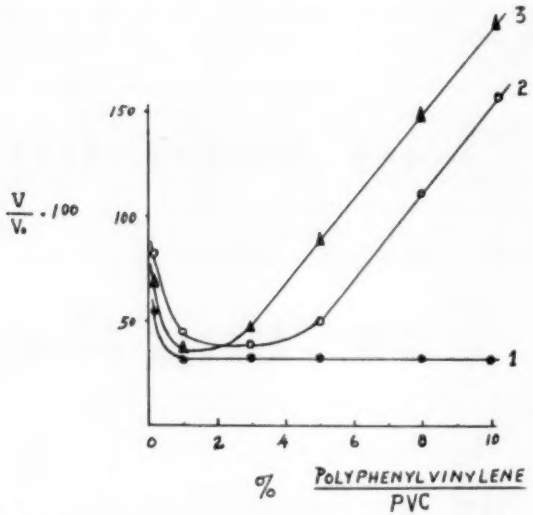

FIG. 2.—Velocity of dehydrochlorination of polyvinylchloride at 175° in an air-stream in the presence of: *1*—polyphenylvinylene (I) prior to heating; *2*—I after 6 hours at 300°; I after 6 hours at 400°.

vinylene I acts as an effective inhibitor within concentration limits of 0.1 to 10% (based upon the weight of PVC); on subsequent treatment at 300°, it initiates breakdown when present in concentrations of 8% or higher, and further heat treatment at 400° results in its initiating decomposition, which sets in even at 6% concentration.

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ROLE OF PRESSURE AND AMOUNT OF BLOWING AGENT IN MOLDING MICROPOROUS FOOTWEAR PARTS *

M. A. Al'bam and A. P. Pisarenko

In the All-Union Film-forming Materials and Artificial Leather Research Institute (VNIIPIK) investigations have been in progress for several years[1] with a view to developing a rational method of production of microporous footwear parts, and to eliminating completely expansion of the parts on removal from the press. It had already been demonstrated that to produce microporous molded parts strictly to the set shape they must be vulcanized with an external pressure not exceeding a certain critical value for each stock formula depending upon the amount of blowing agent, the flowability of the stock and the temperature. However the cause of this marked dependence of the process of molding of microporous parts upon the external pressure was not explained. It was merely suggested that a big part was played by the escape of gas from the cells of the molded rubber.

In order to work out a theoretical basis for the production of molded parts and for the control of the process of pore formation, it was necessary to study the essential nature of the process. For this purpose we studied the kinetics of the process of pore formation and of the escape of gas from a stock in the process of vulcanization.

The method worked out for investigation of the process of pore formation[2] made it possible to study this process under conditions fully corresponding to the actual production conditions of press vulcanization, and to follow simultaneously in one experiment the change in volume of the vulcanization stock and the escape of gas from it. On the basis of these data we plotted the kinetic curves for the processes.

In Figure 1 we show the kinetics of the escape of gas from a stock containing 3% of Porofor ChKhZ-5 blowing agent (Paramethyl urethane benzene sulphonyl hydrazide, *Kauchuk i Rezina*, 1959 *18*, No. 4, p. 9), in vulcanization at 180° and various external pressures on the stock. As may be seen from this drawing, as the external pressure is increased the escape of the gas begins later and proceeds less intensely. From a certain figure for external pressure (5.48 kg/sq ft cm) onwards the escape of gas in the process of vulcanization does not take place at all.

A study of the porous structures of the vulcanized stocks revealed the following. If the rubber is vulcanized with low external pressures, then there is formed a structure with communicating pores, leading to a marked increase in gas permeability. The lower the external pressure during vulcanization, the greater the number of communicating pores. *The escape of the gas from a stock depends upon the formation of these communicating pores and upon their number.*

The alteration in the volume of microporous rubber in the process of vulcanization in the same conditions (Figure 2) showed that at higher external

* Translated by R. J. Moseley from *Kozh.-Obuv. Prom.* 1959, No. 7, 28–33; RABRM translation No. 796.

Figure 1

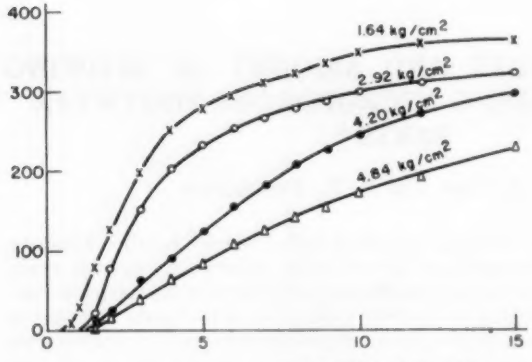

FIG. 1.—Kinetics of escape of gas from a stock containing 3% of Porofor ChKhZ-5 at 180° with various external processes (curves marked with the pressures, 1.64 kg/cm² etc.).

pressures the pore formation begins somewhat later; at lower pressures it proceeds more intensely in the first period. This sort of behavior is quite as to be expected. The later start of pore formation at higher external pressures is caused by the fact that with an increase in the external pressure there is an increase in the amount of gas absorbed by the stock, and therefore the formation of the free gaseous phase begins later. At the same time the lower rate of pore

Figure 2

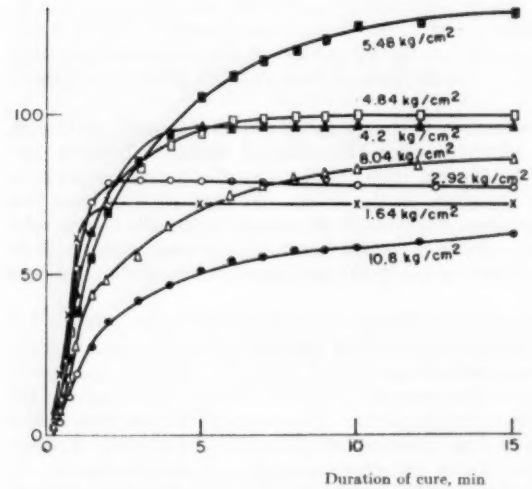

FIG. 2.—Kinetics of increase in volume of a stock containing 3% of Porofor ChKhZ-5 at 180° with various external pressures (curves marked with the pressures, 1.64 kg/sq cm etc.).

formation at higher pressures is explained by the fact that the magnitude of the force causing the pore formation depends upon the difference between the internal and external pressures, and where the other conditions are equal this difference decreases with increase in the external pressure.

But in this way the process of pore formation takes place only in the first period. Thereafter the picture changes sharply. At low external pressures, after the period of relatively rapid pore formation, this process soon stops short (the curve of alteration in volume changes into a horizontal line). The higher the external pressure, the later the pore formation stops. But at external pressures of 5.48 kg/sq cm and above the alteration in the volume lasts over the whole process of vulcanization and does not stop short in the period of time under observation.

Figure 3

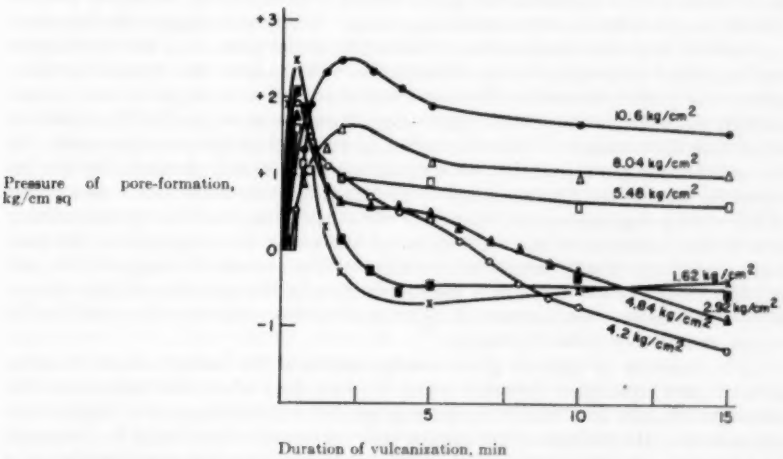

FIG. 3.—Alteration in the pressure of pore formation in a rubber stock containing 3% of Porofor Ch-KhZ-5 during vulcanization at 180° with various external pressures (curves marked with the pressures, 1.64 kg/sq cm etc.)

On comparing Figures 1 and 2 it may be seen that the cutting short of the process of pore formation at low external pressures is connected with the escape of gas from the stock. Obviously with the escape of gas there is a fall in the internal pressure in the pores of the rubber, which is the main cause of pore formation.

As a result of the investigations carried out we calculated the alteration in the internal pressure in the pores of the rubber during vulcanization.

The deformation of a stock in the molding of a prous structure depends upon the difference between the internal pressure of the gas in the pores and the external counterpressure of the press. This difference, which we have called the pressure of pore formation, will indicate the magnitude of the force distending the walls of the pores during pore formation. With absolute equality of the internal pressure of the gas in the pores of the rubber and the external counterpressure of the press the pressure of pore formation is equal to zero. At

this moment the force causing further pore formation in the stock is absent. Reduction of the pressure of pore formation below zero means that the external pressure of the press exceeds the internal pressure of the gases in the rubber and that instead of a force distending walls of the pores there is already a force compressing the microporous article in the mold.

In Figure 3 we show the alteration in the pressure of pore formation during vulcanization with various external pressures. If we look at all three Figures (1, 2 and 3) we may envisage the following picture of the processes which take place.

With an external pressure of 1.64 kg/sq cm at the start of the process (the first 30 sec) there takes place an abrupt leap in the pressure of pore formation as a result of the fact that the magnitude of the external counterpressure is low. At this stage the strength of the stock, which is acquiring a higher temperature all the time, but is still unvulcanized, will be quite low. Deformation of the stock leads to the formation of pores, whose wall thickness decreases proportionally as the volume of the rubber increases. Correspondingly with this there is a reduction in the cross-section of the walls of the pores, i.e., the permissible loading which these pore walls withstand, which leads to the rupture of some part of the pore walls and to the formation of communicating pores, and consequently to the beginning of the escape of gas from the stock (at the 30 sec point). After this the pressure of pore formation is determined by three processes: by the continuing gas formation, causing an increase in this pressure, by the increase in volume and by the escape of gas, leading to its reduction. As a result of the continuing increase in volume of the stock there is all the greater reduction in the thickness of the walls between the pores, new ruptures of the pore walls and there is still further acceleration of the process of escape of the gas. Intense escape of gas leads to a short reduction in the pressure of pore formation, and therefore the increase in volume slows down (after 1 min) and finally ceases completely (after 1.5 min).

The increase in volume of the rubber ceases at the instant when the pressure of pore formation becomes equal to zero, i.e., when the curve cuts the abscissae (Figure 3). Since the internal pressure at this instant is higher than atmospheric, the process of gas escape still continues, which leads to the manifestation of a negative pressure of pore formation, i.e., to the manifestation of a force compressing the rubber on account of excess external pressure developed by the pressure.

Further subsequent increase in the external pressure (cf. the curves corresponding to the pressures 2.29; 4.2; 4.84 kg/sq cm in Figure 3) leads to a slower initial increase in the pressure of pore formation (Figure 2), as a result of which the thickness of the pore walls decreases at a lower rate, the ruptures of the pore walls and the escape of gas begins later, and the number of capillaries formed is cut down. This is aided also by some increase in the strength of the stock as a result of the beginning of vulcanization. Therefore on increasing the external pressure the pressure of pore formation falls more slowly and retains a positive value over a longer period.

The presence of a positive pressure of pore formation over a longer period leads to the process of alteration of volume being cut short later, although it proceeds at a lower rate. The kinetic curves of increase in volume, corresponding to the higher pressures, intersect the curves corresponding to the lower pressures, thanks to which we achieve a big final increase in the volume of the rubber, i.e., a lower specific gravity (Figure 2) of the vulcanized porous article.

On further raising of the external pressure (up to 5.48 kg/sq cm and above)

as a result of the slower increase in the pressure of the pore formation the volume of the rubber increases still more slowly. With this the thickness of the pore walls increases all the more slowly in comparison with the rate of vulcanization, the more the breaking force remains all the time greater than the force developed by the pressure of pore formation, and the pore walls hardly rupture at all. Under these conditions throughout the process of vulcanization up to its end there is practically no escape of gas, the pressure of pore formation remains positive (Figure 3), and the increase in the volume of the rubber does not stop until removal from the press (Figure 2). It must be noted that with these pressures the curves of alteration in volume already do not intersect, and on raising the external pressure the final increase in volume is reduced (the curves for the pressures 5.48 to 10.6 kg/sq cm in Figure 2), i.e., the specific gravity of the article increases.

As may be seen from Figure 3, with low external pressure we very rapidly reach a maximum on the curve of pressure of pore formation, after which the pressure falls rapidly to zero and below. At the moment of extraction from the mold the internal pressure is approximately equal to the atmospheric pressure.

On raising the external pressure the maximum of the pressure of pore formation is reached later, and the subsequent fall-off in pressure takes place more smoothly. But in all cases where at some stage of vulcanization the pressure of pore formation is reduced to zero and below, the result is microporous molded parts which do not change their dimensions on removal from the molds. In those cases where the curve of the pressure of pore formation does not intersect the abscissae up to the end of the vulcanization, i.e., when as a result of the absence of escape of gas the pressure of pore formation maintains positive values, the resulting parts increase in dimensions on removal from the molds.

On reducing the pressure of pore formation below zero the internal pressure is lower than the external counterpressure of the press, but at the same time it may exceed the atmospheric pressure. Therefore on releasing the external pressure at the end of vulcanization, particularly where the pressure of pore formation reaches zero at a relatively late point in vulcanization, there is set up an excess internal pressure of the gases in the rubber under the atmospheric pressure. Nevertheless thanks to the formation of a certain number of communicating pores on the release of the external pressure there takes place a violent escape of gas from the rubber article, and there is no expansion of the part. Consequently the critical pressure corresponds to the maximum external pressure for which at some stage of vulcanization there are still formed a certain number of communicating pores, ensuring a rapid egress of the excess of gas on releasing the external pressure.

Thanks to the prolonged maintenance of a positive pressure of pore formation during the time of vulcanization with the critical external pressure it is possible to produce under these conditions molded parts with exactly the dimensions given and with the minimum possible specific gravity. Therefore vulcanization with external pressures close to the critical value corresponds to the optimum conditions of vulcanization for the production of light molded microporous parts.

In order to determine the influence of the amount of blowing agent upon the kinetics of molding of microporous rubbers we investigated the processes of escape of gas and of the alteration in volume of stocks containing different amounts of blowing agent. On comparison of the curves of the alteration in the volume of the stock, the escape of gas from it, and the curves of the alteration in the pressure of pore formation corresponding to the course of the process

of pore formation in stocks with different dosages of blowing agent for one and the same external pressure, it became evident that alterations in the course of the curves caused by an increase in the amount of blowing agent, are analogous to the alterations in the course of the curves caused by reduction in the external pressure (Figure 1, 2 and 3). The cause of this lies in the fact that the processes of pore formation and escape of gas depend upon the value of the pressure of pore formation and changes in it. Increase in the pressure of pore formation can be caused by a reduction in the external counterpressure or else by a raising of the internal pressure of the gas. The latter is easily brought about by increasing the dosage of blowing agent. Thus increasing the dosage of blowing agent has for the process of pore formation just the same importance qualitatively as a reduction in the external pressure.

To maintain optimum conditions for vulcanization while altering the dosage of blowing agent it is necessary to alter the external pressure to suit. As has already been demonstrated[1], the optimum external pressure is approximately directly proportional to the dosage of blowing agent.

In order to determine the influence of the dosage of blowing agent upon the resulting specific gravity of molded parts, we compared the process of pore formation of stocks with different amounts of blowing agent under optimum conditions of vulcanization. With the stocks used for producing light microporous soles, the volume of the mix increases with amounts of Porofor ChKhZ-5 of 1, 3 and 5 parts by weight (misprints in original, Translator) with the optimum pressure by 84,100 and 122%. Thus the degree of porosity and the specific gravity of the molded parts are not proportional to the amount of blowing agent. But when using stocks with high deformation during vulcanization the increase in the amount of blowing agent may somewhat reduce the specific gravity of the molded parts. The use of stocks with large amount of blowing agent also ensures the possibility of working at higher external pressures; in this case small fluctuations in pressure will not be sharply reflected in alterations in the process of pore formation. An investigation of the structures of the resulting vulcanizates showed that with large dosages of blowing agent we get also finer and even more porosity. Therefore in the production of light molded microporous rubbers it is advisable to employ larger amounts of blowing agent.

In determining in detail the technological parameters of vulcanization of light molded microporous rubber soles it became evident that to ensure good external appearance and uniform porosity it is necessary to carry out at the start of the process a brief molding under high pressure with a smooth reduction of the pressure to an optimum low pressure figure, at which the vulcanization is carried to completion. But in this case the decisive factor in the production of molded soles with minimum specific gravity is the proper selection of the low pressure figure. Therefore we shall deal in conclusion with this question, since it is most simple in practice to establish the figure for the optimum low pressure.

For this purpose we have to carry out some preliminary experiments with consecutive alteration of the low pressure figures by plotting, with the aid of the movement apart of the platens of the press, the kinetic curves of the alteration in the volume of the rubber stock in vulcanization. The pressure corresponding to the curve when with the presence of a horizontal portion of the curve we attain the maximum increase in volume proves to be the optimum pressure for the production of molded parts from the given stock at the given temperature (e.g., the pressure 4.84 kg/sq cm on Figure 2). At the same time further

raising of the low pressure figure leads to a complete disappearance of the horizontal portions of the curve (the curve for the pressure 5.48 kg/sq cm on Figure 2) and to the production of parts which expand on extraction from the molds. If in carrying out the preliminary experiments we find in the very first experiment conditions under which the parts expand on extraction from the molds then subsequent experiments should be carried out lowering the figure of the low pressure.

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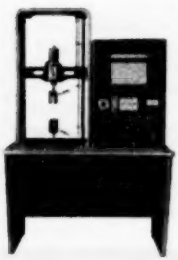

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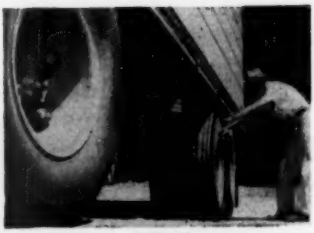

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